

Chemorheology of Aqueous-Based Alumina–Poly(vinyl alcohol) Gelcasting Suspensions

Sherry L. Morissette* and Jennifer A. Lewis*

Department of Materials Science and Engineering and the Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

A new gelcasting system based on aqueous-based alumina–poly(vinyl alcohol) (PVA) suspensions cross-linked by an organotitanate coupling agent has been developed. The chemorheological properties of this system exhibited a strong compositional dependence. A sol–gel phase diagram was established, which yielded the critical titanium concentration ($[Ti]_c$) required for gelation at a given PVA volume fraction as well as the minimum PVA volume fraction ($\phi_{PVA}^{min} = 0.0245$) and titanium concentration ($[Ti]_{min} = 9.984 \times 10^{-4}$ g of Ti/mL) below which gelation was not observed irrespective of solution composition. The gelation time of suspensions of constant PVA volume fraction (ϕ_{PVA}^{soln}) decreased with increased cross-linking agent concentration, temperature, and solids volume fraction. The steady-state viscosity and elastic modulus of polymer solutions ($\phi_{PVA}^{soln} = 0.05$) of varying $[Ti]$ were well described by the percolation model, giving scaling exponents of 0.84 and 1.79, respectively. The steady-state elastic modulus of gelcasting suspensions, which provided a measure of their handling strength in the as-gelled state, increased with increased solids volume fraction.

I. Introduction

GELCASTING is a facile method for fabricating complex, three-dimensional bodies assembled from dense colloidal suspensions. It uses systems of low organic content, which undergo gelation either via polymerization of monomeric species^{1–3} or cross-linking of existing polymeric species in solution.⁴ Gelcasting overcomes many limitations associated with forming methods, such as injection molding (e.g., long removal times and/or flaw generation during binder thermolysis) and slip casting (e.g., slow casting rates, inadequate strength for green machining) suitable for complex shape fabrication^{2,5} by offering short molding times (on the order of several minutes), high yields, high green strength, and low-cost machining.^{1–3} Despite these promising features, however, few fundamental studies have been conducted to determine the effects of composition on the chemorheological properties of gelcasting systems.

Poly(vinyl alcohol) (PVA) in semidilute aqueous solutions readily forms chemical^{6–8} (e.g., by using glutaraldehyde) or physical gels^{9–11} because of hydrogen bonding and/or interactions of hydroxy groups via ion complexation. Cross-linking PVA by the incorporation of an organotitanate coupling agent has been exploited previously by Lewis and co-workers¹² to improve the properties of organocement composites and offers a promising new approach for fabricating gelcast ceramic com-

ponents. Its appeal results from both the widespread use of PVA as a processing aid in ceramics manufacturing (e.g., as a binder in feedstock for dry and cold isostatic pressing) and its good gelforming capabilities.

Gelation, the transition from a liquidlike (sol) to solidlike (gel) behavior, was first described by the mean-field theory of Flory^{13,14} and Stockmayer¹⁵ and subsequently related to percolation theory by Stauffer¹⁶ and DeGennes.¹⁷ A gelling system consists of a solution of discrete species that undergo growth (e.g., monomers \rightarrow network polymers, colloidal particles \rightarrow aggregated network, or linear polymers \rightarrow network polymers) as gelation proceeds. Such species grow until at least one cluster, known as a percolating (or spanning) cluster, reaches a critical size on the order of the sample dimensions, signifying the formation of a gel. The sol–gel transition induces a dramatic change in viscoelastic properties of the system, as illustrated schematically in Fig. 1. The increase in apparent viscosity (η_{app}) with time, prior to its divergence to infinity at the gel point, reflects the structural changes described above. However, if growth is arrested because of depletion of reactant or cross-linking species prior to gel formation, the system remains in the liquid state, and its apparent viscosity plateaus to a steady-state value, η_{equil} . Beyond the gel point, additional linkages can form between growing clusters that strengthen the gel network, as reflected by the coincident increase in the elastic modulus to a steady-state value (G'_{equil}).

Gelation has been studied extensively in related systems, including cross-linkable polymer solutions,^{6,9,18–20} aggregating colloidal suspensions,^{21–23} and sol–gel ceramics,²⁴ with the goal of understanding critical behavior near the sol–gel transition. For example, Allain and Salome²⁰ and Klaveness *et al.*¹⁹ have investigated the steady-state viscosity and elastic modulus of hydrolyzed polyacrylamide solutions of varying chromium(III) cross-linking concentrations and have found that the critical exponents of these rheological properties are in good agreement with scalar percolation predictions. Kjøniksen and Nyström⁶ have studied the time-dependent growth of viscoelasticity during chemical gelation of semidilute PVA solutions cross-linked with glutaraldehyde as a function of varying

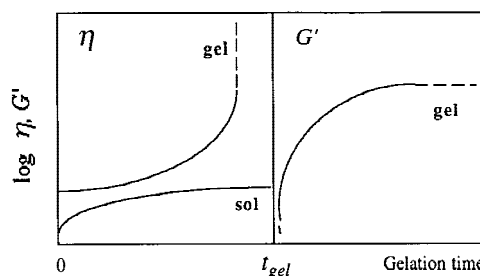


Fig. 1. Schematic illustration of rheological property evolution as a function of gelation time for gelling systems, where η is the apparent viscosity and G' the elastic modulus (adapted from Ref. 28). (Note: Incomplete gelation leads to a sol phase whose apparent viscosity approaches a steady-state value with time.)

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polymer and cross-linker concentrations and have found that the critical exponents decrease with increasing PVA concentration where the best agreement with scalar percolation predictions is exhibited in the incipient semidilute regime. Rueb and Zukoski²² have studied the viscoelastic properties of octadecyl silica particles in decalin and tetradecane during temperature-induced gelation and have found that G'_{equil} increases in a power-law manner with solids volume fraction as predicted for percolating networks.^{24,25} However, surprisingly little attention has been given to the study of more-complex systems, such as gelcasting suspensions, where independent treatment of polymeric and colloidal phases may no longer be suitable.

In this article, the chemorheological properties of aqueous-based alumina–PVA suspensions cross-linked with an organotitanate coupling agent were investigated using stress viscometry and oscillatory measurement techniques. The gelation behavior of PVA solutions with varying cross-linking agent concentration was examined first, and served as a benchmark for understanding the role of solid-filler additions. The observed solution gelation behavior was in good agreement with that described above for other semidilute cross-linkable polymer solutions. However, unlike colloidal gels, whose mechanical properties display a power-law dependence on solids volume fraction, G'_{equil} of gelcasting suspensions exhibited a nearly linear dependence on solid-filler content at low volume fractions (<0.3) prior to diverging to infinity as the maximum solids volume fraction (~ 0.6) was approached. Tailoring the gel strength of such components, therefore, can be best achieved by modifying either the properties of the polymeric (matrix) gel or its filler content.

II. Experimental Procedure

(1) Materials System

Al_2O_3 powder (AKP-30, Sumitomo Chemical Co., New York) with a mean particle size of $0.36 \mu\text{m}$ served as the ceramic phase. An aqueous solution of ammonium poly(methacrylate) (APMA, Darvan C, R.T. Vanderbilt Co., Inc., Norwalk, CT) was used as the dispersant. Partially hydrolyzed PVA (Kuraray International Corp., New York) with a degree of hydrolysis of 80.8 mol% and an average molecular weight of 28 700 g/mol was used as the binder phase. The cross-linking agent for PVA contained 8.3% titanium by weight (Tyzor TE, DuPont Chemicals, Deepwater, NJ). The cross-linking agent consisted of a 25 wt% solution (in isopropyl alcohol) of various organotitanate chelates, with at least one component having the cage structure depicted in Fig. 2(a). According to the product literature, Tyzor TE is not highly susceptible to hydrolysis and, hence, is compatible with cross-linkable materials at room temperature. Cross-linking reactions can be initiated either by increasing the temperature above 100°C or by adjusting the solution pH in the range of 6–10. The proposed cross-linking reaction between partially hydrolyzed PVA and Tyzor TE is illustrated in Fig. 2(b). Gülgün *et al.*²⁶ have studied this reaction in spin-coated PVA films prepared under ambient conditions using X-ray photoelectron spectroscopy (XPS) and have verified the formation of $\text{C}_{\text{PVA}}\text{--O--Ti--O--C}_{\text{PVA}}$ bonds. They also have observed rapid gelation at room temperature over a pH range much broader than originally reported.

(2) Suspension Preparation

Ceramic suspensions were prepared by adding an appropriate volume fraction of Al_2O_3 powder ($\phi_{\text{Al}_2\text{O}_3} = 0.01\text{--}0.45$) to an aqueous solution containing 3 mg of APMA/(g of Al_2O_3). Suspensions were ultrasonicated (Model 550 Sonic Dismembrator, Fisher Scientific, Itasca, IL) at 1 s pulsed intervals for 150 s and subsequently magnetically stirred for 12 h to allow dispersant adsorption onto Al_2O_3 powder surfaces. An appropriate amount of PVA stock solution, prepared by dissolving PVA in deionized (DI) water under ambient conditions, was then added to each suspension. Suspensions were

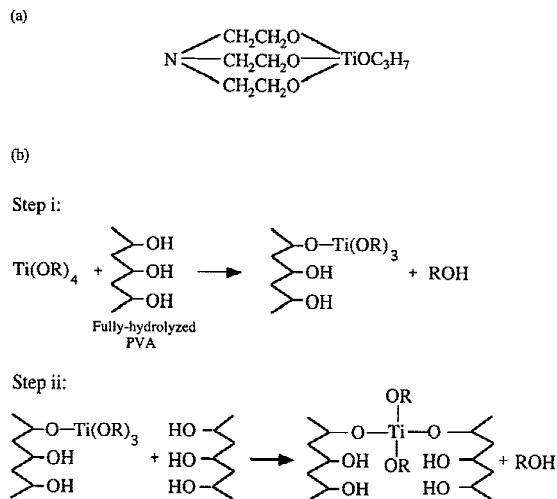


Fig. 2. Schematic illustrations of (a) the representative chemical structure for the organotitanate coupling agent, Tyzor TE, and (b) the proposed cross-linking reaction between Tyzor TE and PVA (adapted from Ref. 12).

concentrated to the desired $\phi_{\text{Al}_2\text{O}_3}$ by forced solvent evaporation using flowing nitrogen. The pH of each suspension was adjusted to 8.5 ± 0.1 using HNO_3 or NaOH . All volume fractions reported were calculated based on the initial volume of each constituent added.

Corresponding polymer solutions of varying PVA volume fraction ($\phi_{\text{PVA}}^{\text{soln}}$) were prepared by diluting the PVA stock solution and adjusting its pH to 4.0 ± 0.1 using HNO_3 or NaOH . Difficulties associated with the respective instabilities of the polymer solutions at pH 8.5 and the dispersant at pH 4.0 prevented rheological measurements from being conducted under identical conditions, which may affect direct comparison between system behavior in the absence and presence of Al_2O_3 particles.

Following the procedure described above, samples were equilibrated at the test temperature and gelation of both polymer solutions and gelcasting suspensions was induced by rapidly stirring in an appropriate amount of the organotitanate cross-linking agent. The titanium concentration ($[\text{Ti}]$) was determined from the known amount of Tyzor TE added. The cross-link density was assumed to be proportional to $[\text{Ti}]$. The phase behavior, rheological measurements, and gelcasting experiments described below were conducted immediately upon the introduction of the cross-linking agent. A representative process flow diagram is provided in Fig. 3.

(3) Phase Behavior

The phase behavior of both polymer solutions and gelcasting suspensions was probed as a function of cross-linking agent concentration. Polymer solutions of varying PVA volume fraction (ϕ_{PVA}) and cross-linking agent concentration as well as gelcasting suspensions ($\phi_{\text{PVA}}^{\text{soln}} = 0.05$) of varying solids volume fraction and cross-linking agent concentration were cast into sealable 50 mL vials and allowed to age undisturbed for 120 h at 22°C . Upon aging, phase formation (i.e., sol or gel) was characterized by visual inspection of the interface motion and/or rise of air bubbles in the samples upon tilting.^{19,20}

(4) Rheological Measurements

Gelcasting suspensions and corresponding polymer solutions were characterized using a controlled stress rheometer (Model Rheolgi CS-10, Bohlin, Cranbury, NJ) fitted with either a concentric cylinder (Model C-14 or C-25) or double concentric cylinder geometry. All rheological measurements were conducted at 22°C unless otherwise noted. Most measurements were made with the C-25 cup and bob (bob diameter of 25 mm and gap width of 1.25 mm), which gave a stress range of

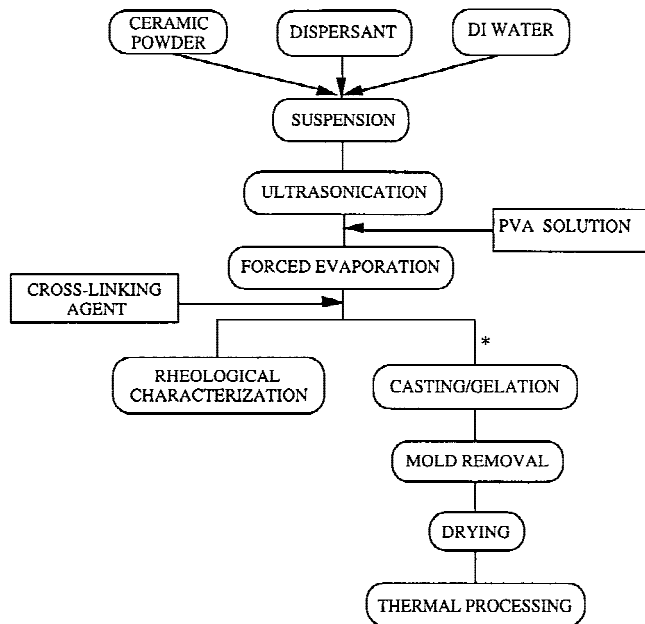


Fig. 3. Process flow diagram for preparation and characterization of gelcasting suspensions. (Note, gelcast bodies are formed by casting the suspension into a mold where gelation occurs *in situ*.)

0.025–240 Pa. However, use of the Couette double-gap cell (gap width of ~2 mm) and the C-14 cup and bob (bob diameter of 14 mm and gap width of 0.7 mm) extended the measurement range to 0.0035–1350 Pa. A specially designed solvent trap filled with DI water was used to minimize solvent loss. Also, a layer of silicone oil ($\eta = 1000$ cP, Brookfield Engineering Laboratory, Inc., Stoughton, MA) was gently placed on the suspension surface to further minimize solvent evaporation. No interaction between the samples and silicone oil was observed.

Stress viscometry was conducted on representative samples, where η_{app} was measured as a function of shear rate in ascending order. Additional measurements were made at a constant shear rate of 0.1 s^{-1} to probe the time-dependent evolution of η_{app} during gelation at varying temperatures. Oscillatory measurements were used to monitor the time-dependent evolution of the shear (elastic and loss) moduli during gelation. These measurements were conducted at a frequency of 0.1 Hz and strain of 3.5%, which lies in the linear viscoelastic region of the samples probed.

III. Experimental Results

(1) Phase Behavior

The phase behavior of the gelcasting system in the absence of solids depended on ϕ_{PVA} and cross-linking agent concentration, as outlined in the phase diagram shown in Fig. 4. The dashed curve represents the phase boundary between the solution (sol) and gel phases, thereby defining the critical titanium concentration ($[Ti]_c$) required to induce gelation for a given ϕ_{PVA}^{sol} . The minimum PVA volume fraction (ϕ_{PVA}^{min}) yielding a gel was ~0.025, which corresponded to the critical overlap concentration (ϕ^*) at which individual PVA coils first intertwine (i.e., the dilute to semidilute transition) resulting in a substantial increase in solution viscosity. The ϕ^* value for PVA solutions was experimentally determined from low-shear-solution viscosity measurements.²⁷ The minimum titanium concentration ($[Ti]_{min}$) yielding a gel was $\sim 1 \times 10^{-3}$ g of Ti/mL at $\phi_{PVA}^{sol} > 0.10$. The critical cross-linking concentration at ϕ_{PVA}^{min} was 3.1×10^{-3} g of Ti/mL, which corresponded to ~30 titanium atoms per PVA chain, assuming a number-average PVA molecular weight of 11 200 g/mol (i.e., polydispersity index =

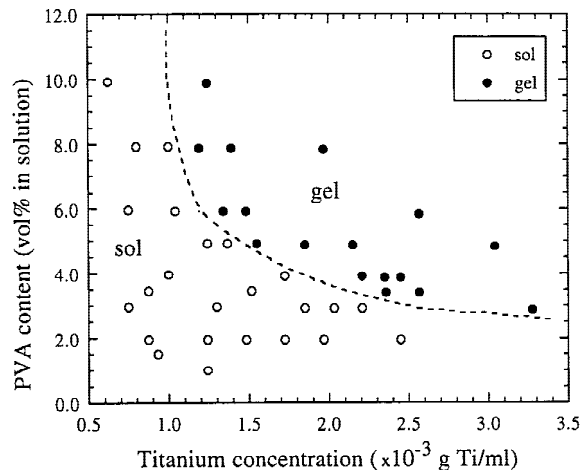


Fig. 4. Phase behavior of polymer solutions in the absence of solids as a function of ϕ_{PVA}^{sol} and $[Ti]$ at 22°C.

2.5). This value was much higher than the prediction of classical theory of one link per chain, and suggests that some intramolecular cross-links form that do not contribute to gelation. Alternatively, it also is possible that not all titanate species react with PVA during gelation. This estimate, however, is in reasonable agreement with the number of cross-links (10 bonds per chain) reported at the gelation threshold for hydrolyzed polyacrylamide cross-linked with chromium(III) ions.²⁰

The influence of solids $\phi_{Al_2O_3}$ on the phase behavior of gelcasting suspensions of constant $\phi_{PVA}^{sol} = 0.05$ and varying cross-linking agent concentration is shown in Fig. 5. For reference, the formulations of representative gelcasting suspensions in suspension clearly affects the sol-gel transition, as revealed by the phase boundary (solid curve) between these single-phase regions. The $[Ti]_c$ required to induce gelation is plotted as a function of $\phi_{Al_2O_3}$ in Fig. 6. $[Ti]_c$ is reduced by ~17% of its initial value as $\phi_{Al_2O_3}$ is increased from 0 to 0.45. The origin of this phenomena is unclear but likely reflects the enhanced reactivity of the cross-linking agent in the presence of the Al_2O_3 particles or possibly direct participation of the particles in the gel structure.

(2) Rheological Properties of PVA Solutions

The apparent solution viscosity (η_{app}^{sol}) as a function of gelation time for $\phi_{PVA}^{sol} = 0.05 \approx 2\phi^*$ of varying cross-linking concentration is shown in Figs. 7(a) and (b). Below $[Ti]_c \approx 1.5 \times$

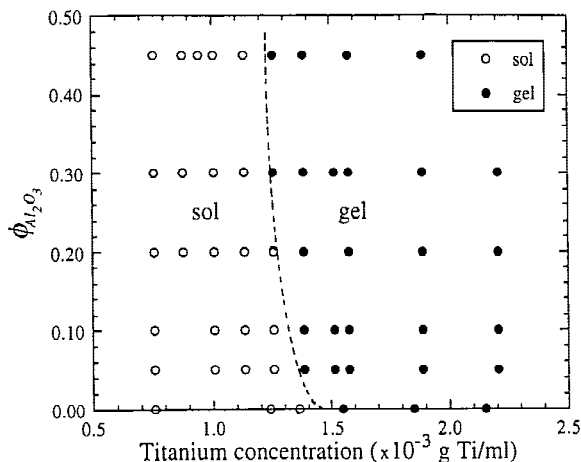


Fig. 5. Phase behavior of gelcasting suspensions of constant $\phi_{PVA}^{sol} = 0.05$ and varying $\phi_{Al_2O_3}$ and $[Ti]$ at 22°C.

Table I. Representative Formulations for Gelcasting Suspensions

Constituent	Function	Volume (percent in suspension)	
		$\phi_{\text{Al}_2\text{O}_3} = 0.10$	$\phi_{\text{Al}_2\text{O}_3} = 0.45$
Alumina	Ceramic	10.00	45.00
Darvan C	Dispersant	0.43	1.93
PVA	Gel-former	4.50 [†]	2.75 [†]
DI water	Solvent	82.92	48.17
Tyzor TE	Cross-linking agent	2.15	2.15

[†]Aqueous PVA volume fraction in each suspension is constant; i.e., $\phi_{\text{PVA}}^{\text{soln}} = 0.05$.

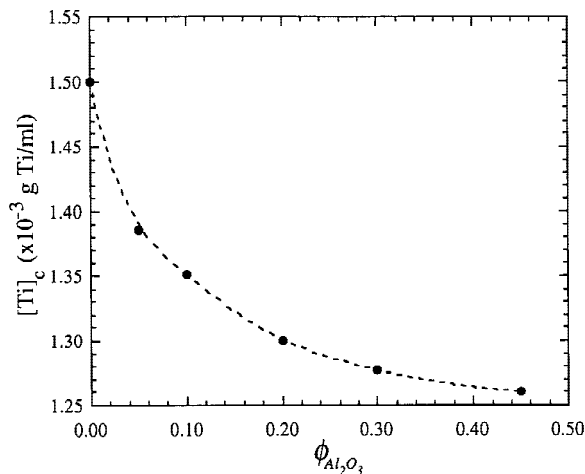


Fig. 6. $[\text{Ti}]_c$ required to promote gelation of gelcasting suspensions of constant $\phi_{\text{PVA}}^{\text{soln}} = 0.05$ and varying $\phi_{\text{Al}_2\text{O}_3}$ at 22°C.

10^{-3} g of Ti/mL, $\eta_{\text{app}}^{\text{soln}}$ increased with gelation time to a steady-state value defined as the equilibrium solution viscosity ($\eta_{\text{equil}}^{\text{soln}}$). The increase in η_{app} reflected the growth of discrete, cross-linked PVA clusters in solution. The onset of steady-state behavior coincided with the cessation of further cross-linking reactions. Not unexpectedly, $\eta_{\text{equil}}^{\text{soln}}$ increased with increased $[\text{Ti}]$, because the final cluster size should scale with cross-link density. $\eta_{\text{app}}^{\text{soln}}$ exhibited a maximum prior to slowly decaying to its equilibrium value, a feature that became more pronounced as the critical cross-linking concentration was approached. This feature may reflect either a disruption to the as-grown cluster structure by the measurement process or a modest contraction of the cluster dimensions as a result of intramolecular cross-link formation. Above $[\text{Ti}]_c$, η_{app} exhibited a period of relatively slow increase followed by a rapid increase as the viscosity diverged to infinity, as shown in Fig. 7(b). The timescale for this process decreased dramatically with increased $[\text{Ti}]$. The gel point (t_{gel}) was difficult to quantify precisely from stress viscometry measurements because of limitations in the maximum measurable viscosity, but could be estimated from the x -axis intercept of the tangent to the viscosity curve at elevated viscosity.

$\eta_{\text{app}}^{\text{soln}}$ as a function of gelation time for constant $\phi_{\text{PVA}}^{\text{soln}} = 0.05$ and $[\text{Ti}] = 2.205 \times 10^{-3}$ g of Ti/mL at varying temperatures is shown in Fig. 8(a). Gelation kinetics were retarded with decreased temperature, such that significant gelation was not observed at 5°C during the duration of these measurements. The observed temperature dependence offers a means of tailoring the processing window of these systems. For example, handling times can be dramatically increased by lowering the temperature prior to casting (after which, the temperature can be increased to initiate the desired rapid gelation).

The time-dependent evolution of the elastic (G') and loss (G'') moduli for a representative PVA solution ($\phi_{\text{PVA}}^{\text{soln}} = 0.05$ and $[\text{Ti}] = 2.205 \times 10^{-3}$ g of Ti/mL) is shown in Fig. 9(a).

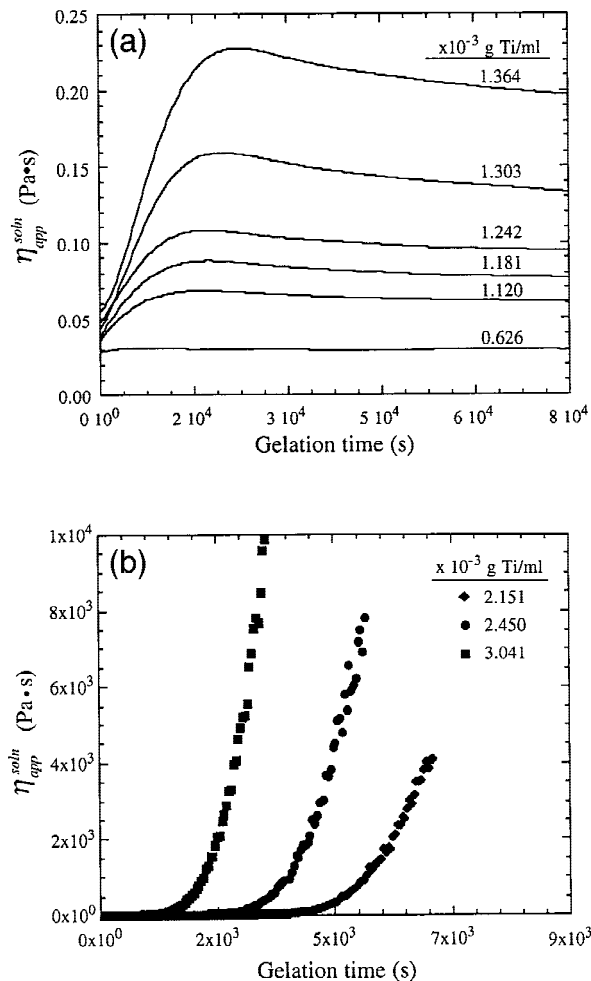


Fig. 7. Plot of $\eta_{\text{app}}^{\text{soln}}$ as a function of gelation time for $\phi_{\text{PVA}}^{\text{soln}} = 0.05$ and varying $[\text{Ti}]$: (a) $[\text{Ti}] < [\text{Ti}]_c$ and (b) $[\text{Ti}] > [\text{Ti}]_c$.

Viscous behavior ($G'' > G'$) was dominant during the initial stage of gelation, when minimal cross-links were formed. Upon increased cross-link formation, both G'' and G' increased, with the latter increasing more sharply until it intersected and then exceeded G'' . The cross-over point ($G' = G''$) has been repeatedly identified in the literature as the gel point (t_{gel}); however, this is true only when $G' \approx G'' \approx \omega^n$, where ω is the angular frequency and $n = 0.5$.^{28–30} The time of intersection generally is similar to the transition time, however, and can be used to evaluate the effects of compositional variations on gelation kinetics. The dependence of gelation time on $[\text{Ti}]$ for constant $\phi_{\text{PVA}}^{\text{soln}} = 0.05$ is shown in the inset of Fig. 9(a), where plotted values correspond to those obtained from the $G' - G''$ crossover and viscosity data (intercepts of the tangent of the curves at $\eta_{\text{app}}^{\text{soln}} = 1000$ Pa·s). The gelation time of these PVA solutions decreased dramatically with increased $[\text{Ti}]$. The two approaches for estimating the gelation time led to significantly different values, where those obtained from the $G' - G''$ crossover consistently were less than those estimated from the viscosity data.

The time-dependent evolution of G' of $\phi_{\text{PVA}}^{\text{soln}} = 0.05$ of varying cross-linking agent concentration is shown in Fig. 9(b). Above the $[\text{Ti}]_c$, G' increased with gelation time to G'_{equil} . The rapid increase in G' with time reflected the buildup of network strength as additional cross-links formed beyond the t_{gel} . The onset of steady-state behavior again coincided with the cessation of further cross-linking reactions. G' was highly sensitive to $[\text{Ti}]$, increasing >2 orders of magnitude from 1 to 200 MPa in response to a twofold increase in $[\text{Ti}]$ from 1.547×10^{-3} g of Ti/mL to 3.041×10^{-3} g of Ti/mL, respectively.

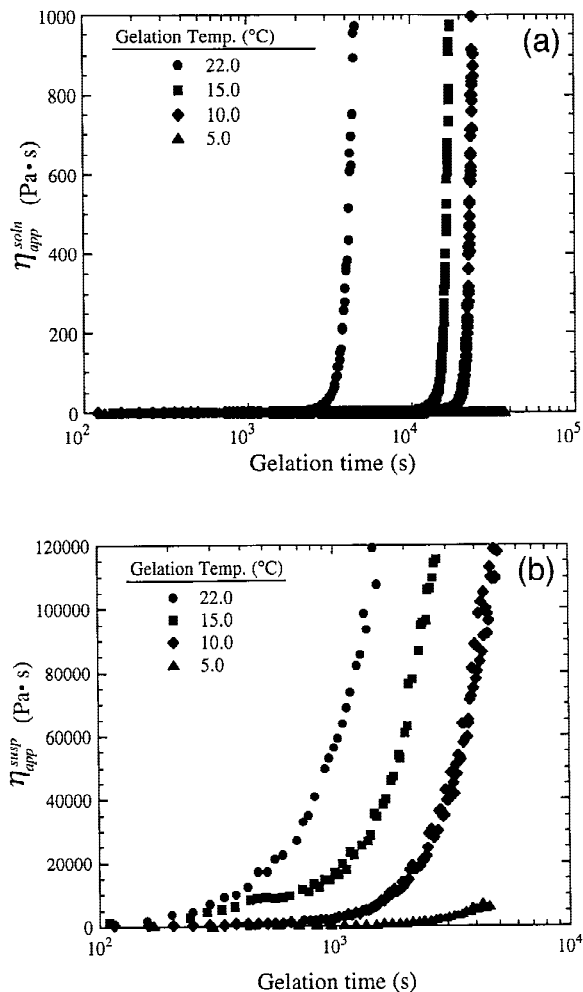


Fig. 8. Semilog plots of η_{app}^{soln} as a function of gelation time for systems held at varying process temperatures: (a) $\phi_{PVA}^{soln} = 0.05$ and $[Ti] = 2.205 \times 10^{-3}$ g of Ti/mL and (b) $\phi_{Al_2O_3} = 0.45$, $\phi_{PVA}^{soln} = 0.05$, and $[Ti] = 2.205 \times 10^{-3}$ g of Ti/mL.

(3) Rheological Properties of Al_2O_3 -PVA Suspensions

η_{app}^{susp} as a function of shear rate for gelcasting suspensions ($\phi_{Al_2O_3} = 0.45$) of $0 \leq \phi_{PVA}^{soln} \leq 0.10$ measured in the absence of cross-linking additions is shown in Fig. 10. The observed increase in η_{app} with increased ϕ_{PVA} mainly reflected changes in solution viscosity, as evidenced by a constant value of the low-shear relative viscosity of 600 ± 100 Pa·s for all suspensions evaluated. At shear rates typical of casting (10 s^{-1}),³¹ the apparent suspension viscosities ranged from 0.1 to 1.0 Pa·s for the ϕ_{PVA} values investigated. Although each suspension has the fluidity ($\eta_{app}^{soln} < 2.0$ Pa·s at 10 s^{-1}) necessary to ensure good mold filling,³² additional measurements were confined to suspensions containing $\phi_{PVA}^{soln} = 0.05$, which corresponded to $2\phi^*$.

The apparent suspension viscosity as a function of gelation time is plotted in Fig. 11(a) for gelcasting suspensions of constant $\phi_{PVA}^{soln} = 0.05$ and $[Ti] = 2.51 \times 10^{-3}$ g of Ti/mL in solution, where $[Ti] > [Ti]_c$, and varying solids volume fraction. The behavior of the corresponding PVA solution also is shown in Fig. 10(a) for comparison. The basic features of these curves were not altered by the presence of the Al_2O_3 filler particles; however, the gelation kinetics were enhanced with increased $\phi_{Al_2O_3}$.

The temperature effects on gelation behavior of gelcasting suspensions of constant $\phi_{Al_2O_3} = 0.45$, $\phi_{PVA}^{soln} = 0.05$, and $[Ti] = 2.205 \times 10^{-3}$ g of Ti/mL are shown in Fig. 8(b), where the apparent viscosity is plotted as a function of gelation time. The trends are similar to those observed for polymer solutions;

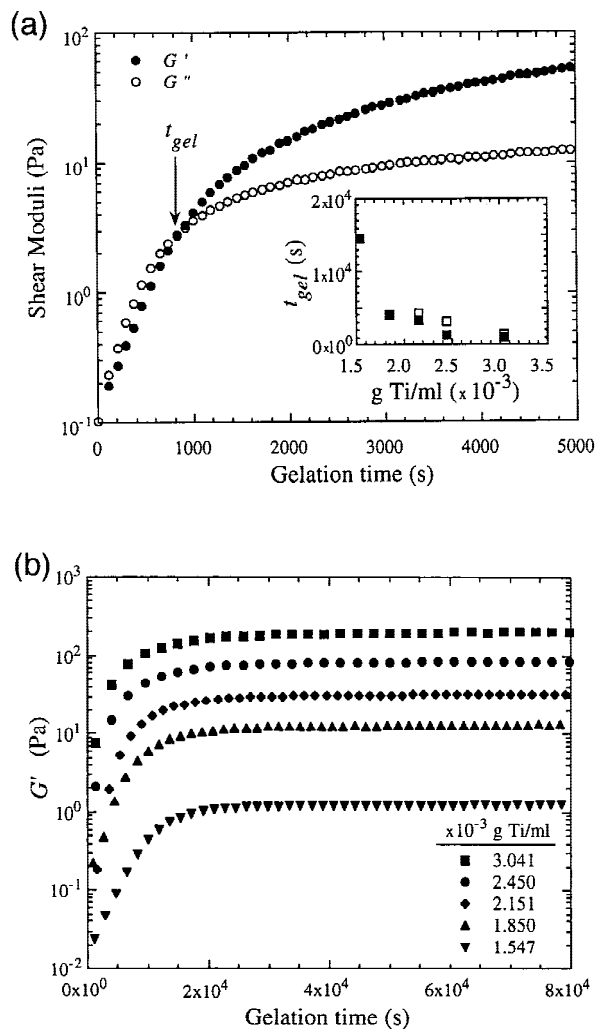


Fig. 9. Evolution of viscoelastic properties during gelation: (a) dependence of G' and G'' on gelation time for a representative $\phi_{PVA}^{soln} = 0.05$, $[Ti] = 2.205 \times 10^{-3}$ g of Ti/mL and (b) dependence of G' on gelation time for $\phi_{PVA}^{soln} = 0.05$ and varying $[Ti]$. (Note: Inset depicts the dependence of gelation time on $[Ti]_c$ evaluated by (filled symbols) $G' - G''$ crossover and (open symbols) viscosity data.)

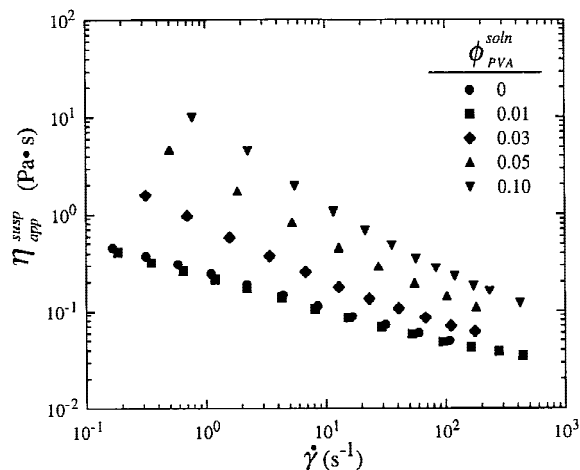


Fig. 10. log-log plot of η_{app}^{susp} as a function of shear rate ($\dot{\gamma}$) for $\phi_{Al_2O_3} = 0.45$ and varying ϕ_{PVA}^{soln} .

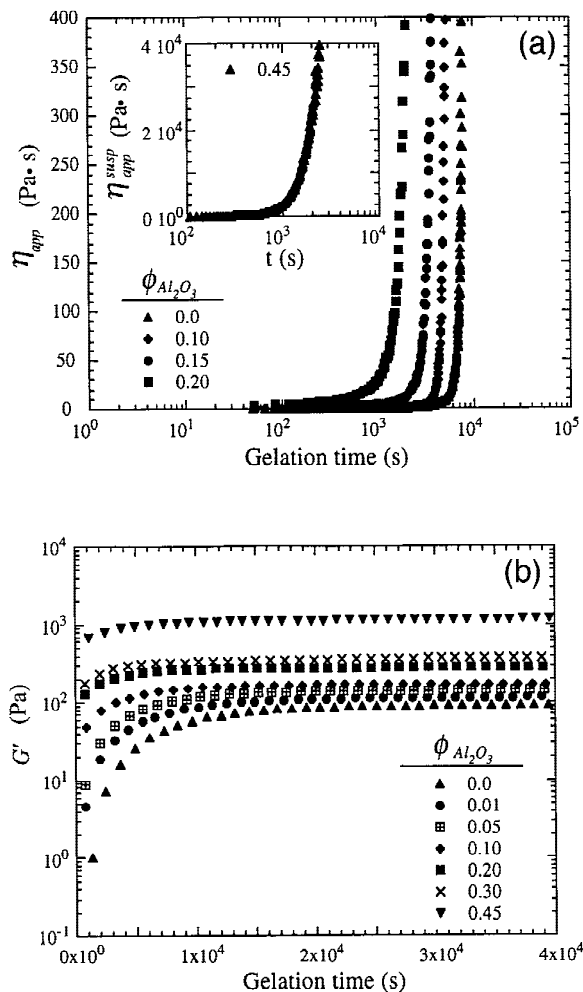


Fig. 11. Evolution of viscoelastic properties during gelation: (a) η_{app}^{susp} and (b) G' as a function of gelation time for gelcasting suspensions of constant $\phi_{PVA}^{soln} = 0.05$, $[Ti] = 2.271 \times 10^{-3}$ g of Ti/mL, and varying solids loading.

i.e., the gelation time increased with decreased temperature. However, unlike the pure solution behavior, a modest increase in η_{app} with gelation time was detected for these suspensions at 5°C. Because of the measured effects of Al_2O_3 filler particles on sol-gel phase behavior under ambient conditions (refer to Fig. 4), such differences were not unexpected at reduced temperatures.

The influence of solids $\phi_{Al_2O_3}$ on the time-dependent evolution of G' for gelcasting suspensions of constant $\phi_{PVA}^{soln} = 0.05$ and $[Ti] = 2.51 \times 10^{-3}$ g of Ti/mL, where $[Ti] > [Ti]_c$, is shown in Fig. 11(b). For comparison, the behavior of the corresponding PVA solution ($\phi_{Al_2O_3} = 0$) also is shown in Fig. 11(b). The presence of solid filler particles altered the mechanical properties of the starting suspensions and final gels, as evidenced by the respective increases in their initial elastic modulus (G'_0) and G'_{equil} with increased $\phi_{Al_2O_3}$. In contrast to the behavior observed for polymer solutions, G' of the suspensions exceeded G'' throughout the gelation process. This interesting feature prevented the detection of t_g from measurements of the $G'-G''$ cross-over.

The effects of $\phi_{Al_2O_3}$ and $[Ti]$ on the gelation kinetics of suspensions with constant $\phi_{PVA}^{soln} = 0.05$ are shown in Fig. 12, where the plotted values correspond to those obtained from viscosity data (intercepts of the tangent of the curves at $\eta_{app} = 1000$ Pa·s). The gelation time observed for polymer solutions in the absence of filler additions is included for comparison. These data suggest that gelation was suppressed by the inclusion of solid fillers at low volume fractions ($\phi_{Al_2O_3} \leq 0.10$).

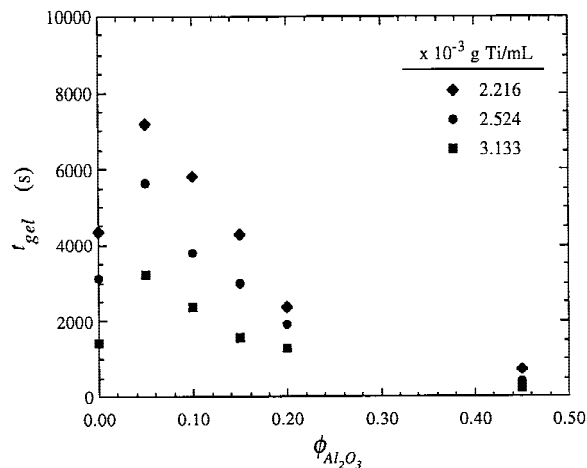


Fig. 12. Plot of gelation time as a function of $\phi_{Al_2O_3}$ for gelcasting suspensions of constant $\phi_{PVA}^{soln} = 0.05$ and varying $[Ti]$.

However, differences between solution pH in the absence and presence of solids complicates the interpretation of these results. Confining the analysis only to suspension behavior, it is clear that t_{gel} decreased significantly with increased $\phi_{Al_2O_3}$ over the range of solids loadings evaluated. Moreover, for systems of constant $\phi_{Al_2O_3}$, t_{gel} decreased with increased $[Ti]$ in a manner similar to the observed solution behavior.

IV. Discussion

The experimental results clearly show that the chemorheological properties of gelcasting systems exhibit a strong compositional dependence. First, the effect of cross-linking agent concentration on the steady-state apparent viscosity and elasticity of polymer solutions is discussed within the framework of percolation theory. Second, the effect of solids volume fraction on gelation behavior is analyzed. Third, the impact of these observations on gelcasting of advanced ceramics is discussed, and strategies are offered for optimizing this important new route for fabricating complex-shaped components.

(1) Gelation of PVA Solutions

The sol-gel transition described in terms of critical phenomena provides power-law behavior for the steady-state viscosity (η_{equil}) before t_{gel} and for G'_{equil} beyond it:

$$\eta_{equil} = \eta_{equil,0}[(p_c - p)/p_c]^{-\kappa} \quad (1)$$

$$G'_{equil} = G'_{equil,0}[(p - p_c)/p_c]^\theta \quad (2)$$

where p is the fraction of cross-links formed, p_c the critical fraction of cross-links formed at t_{gel} , and κ and θ power-law scaling exponents. Allain and Salome²⁰ have shown in related work that the theoretical parameter p is directly related to the measured cross-link concentration. Assuming the cross-link concentration is proportional to $[Ti]$ in solution and the critical cross-link concentration is related to $[Ti]_c$ following the same dependence, one finds

$$\frac{p - p_c}{p_c} = \frac{[Ti] - [Ti]_c}{[Ti]_c} \quad (3)$$

which can be substituted into Eqs. (1) and (2). The formation of intramolecular cross-links should not alter these expressions, because their proportion is fixed for a given ϕ_{PVA} in solution.²⁰

log-log plots of the steady-state apparent viscosity (η_{equil}^{app}) and G' of polymer solutions ($\phi_{PVA}^{soln} = 0.05$) as a function of $[Ti]$ are shown in Figs. 13(a) and (b), respectively. Power-law fits to the data shown in Figs. 13(a) and (b) yielded exponents of $\kappa = 0.84$ and $\theta = 1.79$ for η_{equil}^{app} and G' , respectively. These exponents were highly sensitive to the chosen value of the critical cross-link concentration, which often was difficult to assess for most gelling systems. Here, $[Ti]_c$ was determined

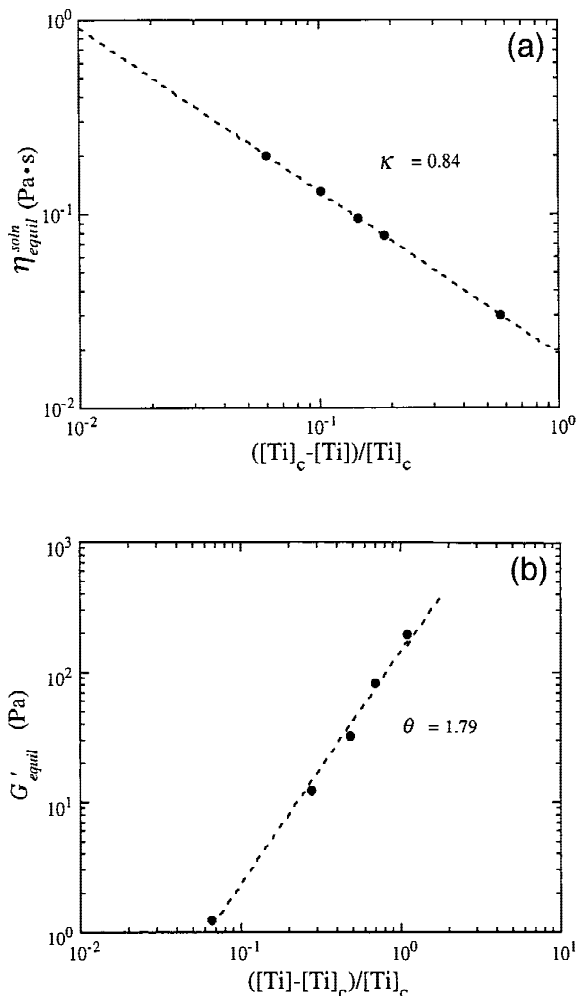


Fig. 13. log-log plots of (a) η_{equil}^{soln} for polymer solutions of constant $\phi_{PVA}^{soln} = 0.05$ as function of varying $[Ti]$, where $[Ti] < [Ti]_c$, and (b) G'_{equil} for polymer solutions of constant $\phi_{PVA}^{soln} = 0.05$ as function of varying $[Ti]$, where $[Ti] > [Ti]_c$.

directly from the phase diagram shown in Fig. 4. The calculated exponents are in good agreement with those predicted by the percolation model (i.e., $\kappa = 0.75$ and $\theta = 1.9$) suggested by DeGennes,¹⁷ which, for example, is based on an analogy between gel elasticity and the conductivity of a random conductor network. Moreover, these values compare favorably with values reported for other polymer-cross-linker systems, such as hydrolyzed polyacrylamide gels cross-linked with chromium(III) ions, where $\kappa = 0.9 \pm 0.2$ (Ref. 20) and $\theta = 1.9 \pm 0.1$ (Refs. 19 and 20). These results provide further support for the use of scalar percolation models for describing sol-gel transitions.

(2) Solids Effects on Gelation

Related empirical studies³³⁻³⁷ have investigated the effects of solid filler particles on the chemorheological and curing/gelation kinetics of cross-linking polyester and epoxy resins. Solids additions are desirable in such systems, because they reduce the cost of molded plastic parts while enhancing their thermal and mechanical properties. Lem and Han³³ found that increased $CaCO_3$, clay, or high-density polyethylene particulate filler additions in an unsaturated polyester resin led to increased shear thinning behavior and curing rates. Similarly, Ng and Manas-Zloczower³⁵ found that SiO_2 additions to an epoxy resin led to an increased elastic modulus of the cured matrix as well as enhanced curing rates. In contrast, Paauw and Pizzi³⁷ examined the effects of five fillers on the cross-linking behavior of unsaturated polyester resins and found, for example, that SiO_2 additions had little effect on curing kinetics.

The addition of Al_2O_3 filler particles to the gelcasting system studied here led to altered chemorheological behavior and to accelerated gelation kinetics. The reduction in $[Ti]_c$ required to induce gelation with increased solids volume fraction suggests that the filler particles could not be considered inert. The dramatic reduction in gelation time with increased solids volume fraction, as determined from rheological measurements, further supported this interpretation. Moreover, the presence of Al_2O_3 filler particles changed the mechanical behavior of the system, as reflected by the increase in G'_{equil} of the gelled network with increased $\phi_{Al_2O_3}$. The solids volume fraction dependence of G'_{equil} was modeled using a modified form of Kerner's equation:³⁵

$$G'_{equil} = G'_{equil,0} \left[1 + \frac{15(1-\nu)}{8-10\nu} \frac{\phi}{\phi_m - \phi} \right] \tag{4}$$

where G'_{equil} is the steady-state elastic modulus of the filled system, $G'_{equil,0}$ the steady-state elastic modulus of the matrix (polymeric gel in the absence of solids), ϕ the volume fraction of Al_2O_3 filler particles, ϕ_m the maximum volume fraction of Al_2O_3 filler particles (~ 0.60), and ν the Poisson's ratio of the matrix. The curves calculated from Eq. (4) using a value of $\nu = 0.36$ for the matrix are plotted with the experimental data in Fig. 14. Two cases were evaluated: (1) the dotted curve corresponds to the calculated fit using a constant value for $G'_{equil,0}$, as measured in the absence of solids, and (2) the dashed curve corresponds to the calculated fit using modified values for $G'_{equil,0}$, as determined using the scaling relation given in Eq. (2), where $[Ti]_c$ was adjusted based on the experimental data given in Fig. 5. An excellent fit to the measured mechanical behavior of the filled gels was obtained when one accounted for the increased $G'_{equil,0}$ of the matrix that resulted because of the reduction in $[Ti]_c$ with increased $\phi_{Al_2O_3}$.

(3) Impact on Gelcasting

Polymer-based gelcasting systems are a viable alternative to those based on *in-situ* polymerization of monomeric systems. This study highlights the importance of suspension composition (i.e., polymer, cross-linking agent, and solids content) and processing temperature on gelation behavior. A minimum polymer concentration in solution (roughly corresponding to ϕ^*) is required to promote gelation. The accompanying increase in solution viscosity that results from the presence of such species does limit the amount of ceramic solids that can be incorporated into the system while continuing to yield a flowable initial suspension. However, use of powders of tailored particle-size distribution should allow processable suspensions at higher solids volume fractions (>0.45) than those explored in

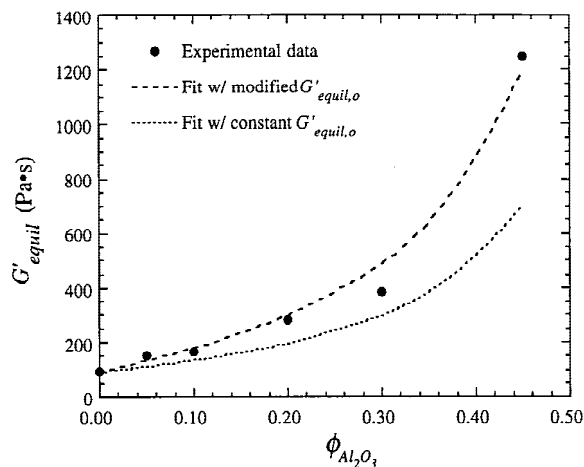


Fig. 14. Plot of G' as a function of solids $\phi_{Al_2O_3}$ for gelcasting suspensions of constant $\phi_{PVA}^{soln} = 0.05$ and $[Ti] = 2.205 \times 10^{-3}$ g of Ti/mL.

the present study. A marked decrease in gelation rates is observed for both the polymer solutions and gelcasting suspensions at reduced temperatures. The strong temperature dependence of the gelation kinetics is considered advantageous, because one can overcome the accelerating effect of solids additions on gelation rates by handling such systems at low temperatures prior to casting. G'_{equil} , which reflects the strength of the as-gelled components, depends strongly on cross-link concentration (i.e., [Ti]) and solids volume fraction. In practice, a high gel strength is desired to facilitate mold release and subsequent handling of the as-formed parts. One can now precisely tailor the gel strength of such components by exploiting the power-law dependence on cross-link concentration as well as the solids volume fraction dependence established by this work.

V. Summary

A new gelcasting system based on aqueous Al_2O_3 -PVA suspensions cross-linked with an organotitanate coupling agent was developed. The phase behavior of both pure polymer solutions and gelcasting suspensions was determined, from which the minimum PVA volume fraction and the critical cross-linking concentration at a given PVA volume fraction needed to promote gelation were established. The addition of Al_2O_3 particles shifted the sol-gel phase transition to increasingly lower critical cross-link concentrations, suggesting that the solid filler was not inert. The chemorheological properties of this system then were investigated, from which the concentration and temperature dependence of important process parameters, such as the suspension viscosity, gelation time, and steady-state elastic moduli, were determined. On the basis of these observations, process guidelines were established for tailoring the behavior of these chemically reactive, colloidal-polymeric suspensions developed principally for fabricating advanced, gelcast ceramic components.

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APPENDIX Definition of Terms Used

G'	Elastic modulus
G''	Loss modulus
G'_0	Initial elastic modulus
G'_{equil}	Steady-state elastic modulus
$G'_{\text{equil},0}$	Initial steady-state elastic modulus
t_{gel}	Gel point
[Ti]	Titanium concentration
$[\text{Ti}]_c$	Critical titanium concentration
$[\text{Ti}]_{\text{min}}$	Minimum titanium concentration
η_{app}	Apparent viscosity
η_{equil}	Steady-state viscosity
$\eta_{\text{app}}^{\text{soln}}$	Apparent solution viscosity
$\eta_{\text{equil}}^{\text{soln}}$	Equilibrium solution viscosity
$\eta_{\text{app}}^{\text{soln}}$	Steady-state apparent viscosity
ϕ_{PVA}	PVA volume fraction
$\phi_{\text{PVA}}^{\text{min}}$	Minimum PVA volume fraction
$\phi_{\text{PVA}}^{\text{soln}}$	PVA volume fraction in solution
$\phi_{\text{Al}_2\text{O}_3}$	Alumina volume fraction
ϕ^*	Critical overlap concentration

References

- O. O. Omatete, M. A. Janney, and R. A. Strehlow, "Gelcasting—A New Ceramic Forming Process," *Am. Ceram. Soc. Bull.*, **70** [10] 1641–49 (1991).
- A. C. Young, O. O. Omatete, M. A. Janney, and P. A. Menchhofer, "Gelcasting of Alumina," *J. Am. Ceram. Soc.*, **74** [3] 612–18 (1991).

- O. O. Omatete, R. A. Strehlow, and C. A. Walls, "Gelcasting of Submicron Alumina, SiAlON, and Silicon Nitride Powders"; in Proceedings of the 37th Sagamore Army Materials Research Conference (Plymouth, MA, 1990).

- S. L. Morissette, P. G. Desai, and J. A. Lewis, "Gelcasting of Al_2O_3 -PVA Suspensions"; presented at the 97th Annual Meeting of The American Ceramic Society, Cincinnati, OH, May 2, 1995 (Science, Technology, and Commercialization of Powder Synthesis and Shape Forming Process Symposium, Poster No. SXIXP-17-95).

- T. J. Graule, W. Si, F. H. Baader, and L. J. Gauckler, "Direct Coagulation Casting (DCC): Fundamentals of a New Forming Process for Ceramics"; pp. 457–61 in Ceramic Transactions, Vol. 51, *Ceramic Processing Science and Technology*, Edited by H. Hausner, G. L. Messing, and S. Hirano. American Ceramic Society, Westerville, OH, 1995.

- A. Kjøniksen and B. Nyström, "Dynamic Light Scattering of Poly(vinyl alcohol) Solutions and Their Dynamic Behavior During the Chemical Gelation Process," *Marmolecules*, **29**, 7116–23 (1996).

- Y. Ikada, Y. Nishizaki, Y. Uyama, T. Kawahara, and I. Sakurada, "Reaction of Poly(vinyl alcohol) with Pentavalent Vanadium Ion" *Polymer Chemistry Edition, J. Polym. Sci.*, **14**, 2251–61 (1976).

- L. I. Moneva and K. R. Ivanova, "A Study of the Gelation of Poly(vinyl alcohol) Solutions Containing Divalent Copper," *Polym. Sci. USSR*, **32** [10] 2054–60 (1990).

- T. Takigawa, M. Takahashi, K. Urayama, and T. Masuda, "Comparison of Model Prediction with Experiment of Concentration-Dependent Modulus of Poly(vinyl alcohol) (PVA) Gels Near the Gelation Point," *Chem. Phys. Lett.*, **195** [5,6] 509–51 (July 31, 1992).

- M. Ohura, T. Kanaya, and K. Kaji, "Gelation Rates of Poly(vinyl alcohol) Solution," *Polymer*, **33** [3] 5044–48 (1992).

- K. Yamaura, K. Karasawa, T. Tanigami, and S. Matsuzawa, "Gelation of Poly(vinyl alcohol) Solutions at Low Temperatures (20° to -78°C) and Properties of Gel," *J. Appl. Polym. Sci.*, **51**, 2041–46 (1994).

- P. G. Desai, J. A. Lewis, and D. P. Bentz, "Unreacted Cement Content in Macro-Defect-Free Composites—Impact on Processing Structure Property Relations," *J. Mater. Sci.*, **29** [24] 6445–52 (Dec. 15, 1994).

- P. J. Flory, "Molecular Size Distribution in Three-Dimensional Polymers. I. Gelation," *J. Am. Chem. Soc.*, **63**, 3083 (1941).

- P. J. Flory, "Constitution of Three-Dimensional Polymers and the Theory of Gelation," *J. Phys. Chem.*, **46**, 132–40 (1942).

- W. H. Stockmayer, "Theory of Molecular Size Distribution and Gel Formation in Branched-Chain Polymers," *J. Chem. Phys.*, **11** [2] 45–55 (1943).

- D. A. Stauffer, "Gelation in Concentrated Critically Branched Polymer Solutions: Percolation Scaling Theory of Intermolecular Bond Cycles," *J. Chem. Soc. Faraday Trans. II*, **72**, 1354–64 (1976).

- P. G. DeGennes, *Scaling Concepts in Polymer Physics*; p. 342. Cornell University Press, Ithaca, NY, 1979.

- M. Tokita, R. Niki, and K. Hikichi, "Critical Behavior of Modulus of Gel," *J. Chem. Phys.*, **83** [5] 2583–86 (Sept. 1, 1985).

- T. M. Klaveness, P. Ruoff, and J. Kolnes, "Kinetics of Cross-Linking of Poly(acrylamide) with Cr(III). Rheological Measurements of the Gelation," *J. Phys. Chem.*, **99**, 8255–59 (1995).

- C. Allain and L. Salome, "Gelation of Semidilute Polymer Solutions by Ion Complexation: Critical Behavior of the Rheological Properties versus Cross-Link Concentration," *Macromolecules*, **23**, 981–87 (1990).

- J. E. Martin, D. Adolf, and J. P. Wilcoxon, "Viscoelasticity Near the Sol-Gel Transition," *Phys. Rev. A: Gen. Phys.*, **39** [3] 1325–32 (Feb. 1, 1989).

- C. J. Rube and C. F. Zukoski, "Viscoelastic Properties of Colloidal Gels," *J. Rheol.*, **41** [2] 197–218 (March/April 1997).

- M. C. Grant and W. B. Russel, "Volume-Fraction Dependence of Elastic Moduli and Transition Temperatures for Colloidal Silica Gels," *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, **47** [4] 2606–14 (1993).

- J. E. Martin, J. P. Wilcoxon, and D. Adolf, "Critical Exponents for the Sol-Gel Transition," *Phys. Rev. A: Gen. Phys.*, **36**, 1803–1810 (1987).

- D. A. Stauffer, A. Coniglio, and M. Adam, "Gelation and Critical Phenomena," *Adv. Polym. Sci.*, **44**, 103–58 (1982).

- M. Gülgün, O. Popoola, and W. Kriven, "X-ray Photoelectron Spectroscopy Studies of Bond Structure Between Poly(vinyl alcohol) and a Titanate Cross-Coupling Agent," *J. Mater. Res.*, **10** [6] 1565–71 (1995).

- S. L. Morissette and J. A. Lewis, unpublished work.

- H. H. Winter, "Polymer Gels, Materials that Combine Liquid and Solids Properties," *Mater. Res. Soc. Bull.*, **16** [8] 44–48 (1991).

- F. Chambon and H. H. Winter, "Linear Viscoelasticity at the Gel Point of a Cross-Linking PDMS with Imbalanced Stoichiometry," *J. Rheol. (NY)*, **31** [8] 683–97 (1987).

- H. H. Winter and F. Chambon, "Analysis of Linear Viscoelasticity of a Cross-Linking Polymer at the Gel Point," *J. Rheol. (NY)*, **30** [2] 367–82 (1986).

- J. A. Reed, *Introduction to the Principles of Ceramic Processing*; p. 381. Wiley Interscience, New York, 1988.

- O. O. Omatete, private communication (Nov. 1997).

- K. Lem and C. D. Han, "Chemorheology of Thermosetting Resins. II. Effect of Particulates on the Chemorheology and Curing Kinetics of Unsaturated Polyester Resin," *J. Appl. Polym. Sci.*, **28**, 3185–206 (1983).

- A. Dutta and M. E. Ryan, "Effects of Fillers on Kinetics of Epoxy Cure," *J. Appl. Polym. Sci.*, **24**, 635–49 (1979).

- H. Ng and I. Manas-Zloczower, "Chemorheology of Unfilled and Filled Epoxy Resins," *Polym. Eng. Sci.*, **33** [4] 211–16 (1993).

- S. H. McGee, "Curing Characteristics of Particulate-Filled Thermosets," *Polym. Sci. Eng.*, **22** [8] 484–91 (June 1982).

- M. Paauw and A. Pizzi, "Some Filler Effects on Cross-Linking of Unsaturated Polyesters," *J. Appl. Polym. Sci.*, **50**, 1287–93 (1993). □