

AFOSR TR 97-0689

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 28 October 1997	3. REPORT TYPE AND DATES COVERED Final Technical Report 1 Aug 96 to 31 Jul 97		
4. TITLE AND SUBTITLE "Acquisition of a Scanning Ultrasound analyzer for Gelation and Drying Studies in Sol-Gel Ceramic Coatings and Monoliths"			5. FUNDING NUMBERS F49620-96-1-0421	
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NA 110 Duncan Avenue, Rm B115 Bolling AFB, DC 20332-8050			10. SPONSORING/MONITORING AGENCY REPORT NUMBER F49620-96-1-0421	
11. SUPPLEMENTARY NOTES none				
12a. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				
19971204 168				
13. ABSTRACT (Maximum 200 words) The overall goal of this research project was to develop a fundamental understanding of how col-loid chemistry influences structure and properties of ceramic monoliths fabricated by sol-gel syn-thesis from colloid suspensions. The specific objective in the first part of the project was to determine how the interaction potential between colloidal particles influenced gel structure and strength. We proposed to do this using Stokesian Dynamics computer simulations and time-dependent ultrasonic measurements of elastic modulus for gels synthesized using various colloidal silica sol concentrations and electrolyte strengths. Detailed negotiations about equipment pricing and capabilities revealed that a simpler experimental method (mechanical rheometry) could be more effective than the proposed ultrasonic technique for elucidating time-dependent gel structure evolution and yielding. With the written permission of Dr. Pechenik, the Program Director, funding allocated for purchasing the ultrasonic device and designated matching funds from Texas A&M University were used to purchase a Paar Physica Universal Dynamic Spectrometer (UDS). During the last year this instrument was successfully purchased installed at Texas A&M University and is already shedding needed light on the gelation kinetics of concentrated colloid suspensions. The following report summarizes our reasons for choosing the UDS and provides an overview of our research findings using the instrument.				
14. SUBJECT TERMS			15. NUMBER OF PAGES 5	
DTIC QUALITY INSPECTED 4			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

Final Report for Project 49820 CH: "Acquisition of a Scanning Ultrasound Analyzer for Gelation and Drying Studies in Sol-Gel Ceramic Coatings and Monoliths".

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Institution: Texas A&M University, Department of Chemical Engineering

Program Director: Dr. Alexander Pechenik.

Synopsis:

The overall goal of this research project was to develop a fundamental understanding of how colloid chemistry influences structure and properties of ceramic monoliths fabricated by sol-gel synthesis from colloid suspensions. The specific objective in the first part of the project was to determine how the interaction potential between colloidal particles influenced gel structure and strength. We proposed to do this using Stokesian Dynamics computer simulations and time-dependent ultrasonic measurements of elastic modulus for gels synthesized using various colloidal silica sol concentrations and electrolyte strengths. Detailed negotiations about equipment pricing and capabilities revealed that a simpler experimental method (mechanical rheometry) could be more effective than the proposed ultrasonic technique for elucidating time-dependent gel structure evolution and yielding. With the written permission of Dr. Pechenik, the Program Director, funding allocated for purchasing the ultrasonic device and designated matching funds from Texas A&M University were used to purchase a Paar Physica Universal Dynamic Spectrometer (UDS). During the last year this instrument was successfully purchased installed at Texas A&M University and is already shedding needed light on the gelation kinetics of concentrated colloid suspensions. The following report summarizes our reasons for choosing the UDS and provides an overview of our research findings using the instrument.

The Paar Physica Universal Dynamic Spectrometer (UDS) is uniquely suited for our research for two reasons. First, the instrument employs a novel air bearing measuring system that provides good stress sensitivity at the low strain amplitudes needed to non-invasively study gel structure. Second, the UDS is also capable of performing rheological measurements using either controlled stresses or controlled strain rate. This capability is essential for characterizing colloidal gel structure and properties because, depending of their aggregation state, these materials display mechanical behavior ranging from those characteristic of simple liquids to those found in hard elastic solids with yield stresses.

During the last year we successfully installed the UDS at Texas A&M and used it to perform time-dependent oscillatory shear measurements at fixed oscillation frequency in gelling aqueous silica suspensions. Gelation was produced in all cases by destabilizing the interparticle electrostatic potential by addition of fixed amounts of salts. Fourier decomposition of the time dependent complex modulus G^* allowed the storage (elastic) and loss (viscous) moduli, G' and G'' , respectively to be deduced. Figure 1 summarizes typical results. At early times the colloidal sol is a viscous liquid, so the elastic modulus is much smaller than the loss modulus. As the material gels and a three-dimensional network structure develops, elasticity increases. The time at which the two moduli intersect (around 800 seconds in this case) is the theoretical gel-time of the material. Importantly, we've found that this time coincides with a previously unknown fall-off in the actual shear strain delivered to the material. We believe that this fall-off in strain is a consequence of the rapid cross-linking of particles as the material changes from a liquid-like consistency to a solid-like one, which offers more resistance to the imposed straining. This finding provides a useful new method for establishing the gelation time of a colloidal suspension.

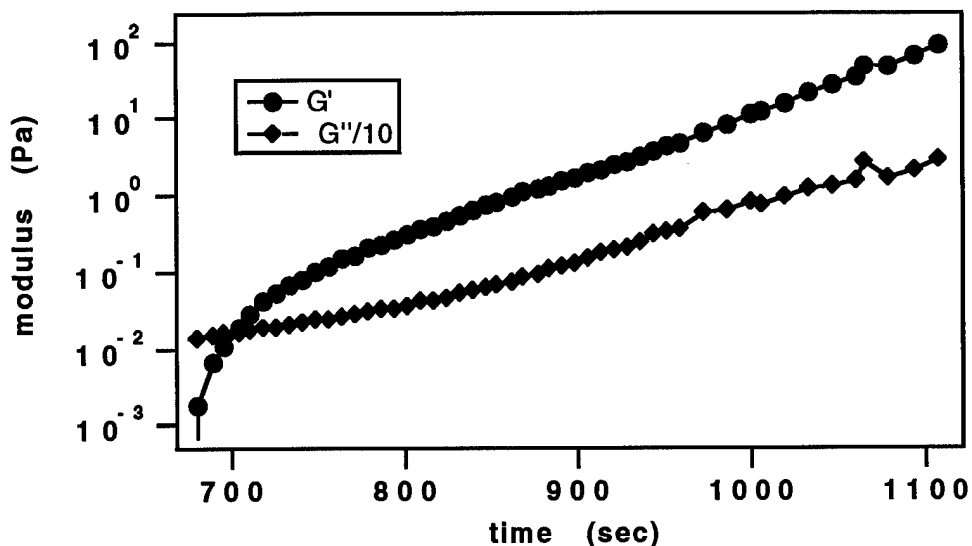


FIGURE 1. Time-dependent storage and loss moduli of 40 volume percent colloidal silica suspension in deionized water. At time $t=0$, 0.18M ammonium formate was added to the suspension to induce gelation.

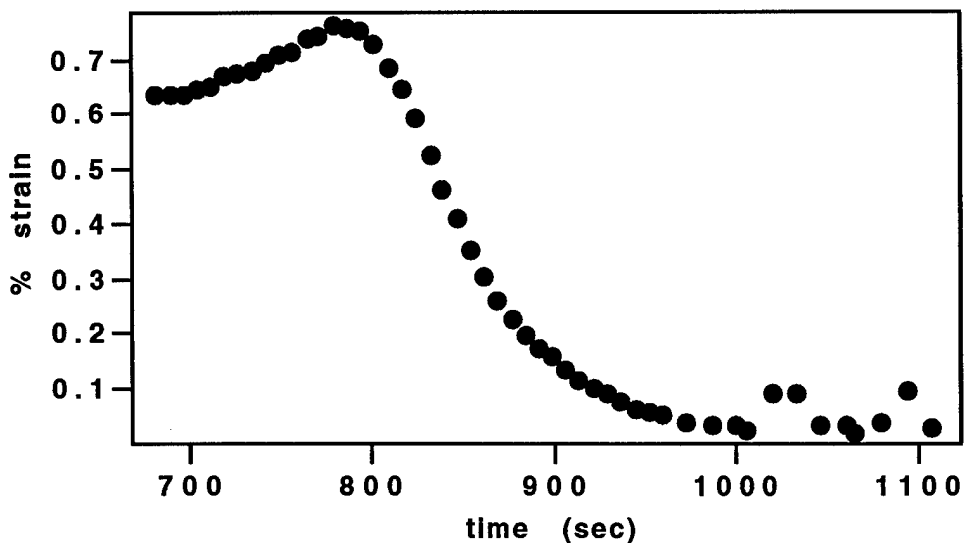


FIGURE 2. Actual strain amplitude delivered to material in Fig. 1 for a command strain of 0.6%.

Experimental gelation times determined in this manner revealed two distinct aggregation mechanisms, depending on electrolyte concentration. At high electrolyte concentrations (above

0.3 M) gelation occurred rapidly and the gelation time t_g scales with concentration of electrolyte as $t_g \sim c^{-6.0 \pm 0.3}$ (Figure 3). On the other hand, at low electrolyte concentrations (below 0.3 M) a much slower gelation process is seen in which a weaker power-law dependence on electrolyte concentration $t_g \sim c^{-3.0 \pm 0.2}$ is observed (Figure 4). The gel-time concentration scaling in neither regime is consistent with predictions from Stokesian dynamics simulations $t_g \sim c^{-0.5 \pm 0.2}$, in which diffusion is known to be dominant. It seems apparent then that two specific types of network reactions can occur in these systems, the origin of which is at present not fully resolved. Future work on this project will focus on the detailed chemical processes involved in the two gelation mechanisms identified in aqueous silica suspensions. Preliminary experiments using

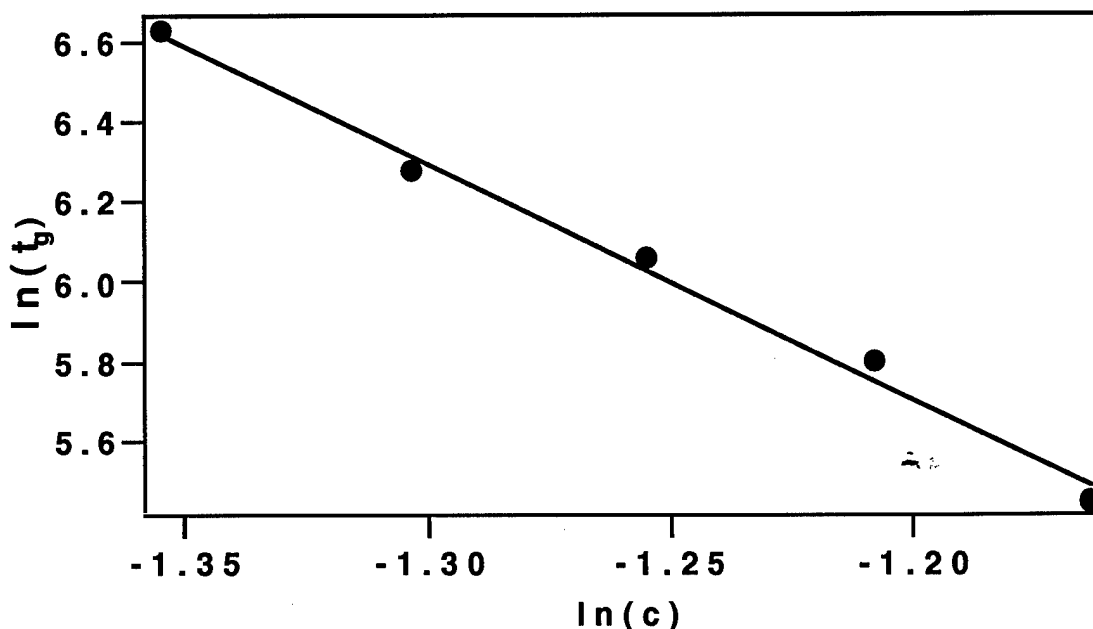


FIGURE 3. Gelation time for concentrated aqueous silica suspensions versus electrolyte concentration [“Rapid gelation regime”].

aqueous polystyrene latex suspensions suggest that only the slower of the two features found in the silica-based colloidal suspensions are universal. That neither feature is predicted by Stokesian dynamics simulations employing DLVO potential functions suggests that more complex potential

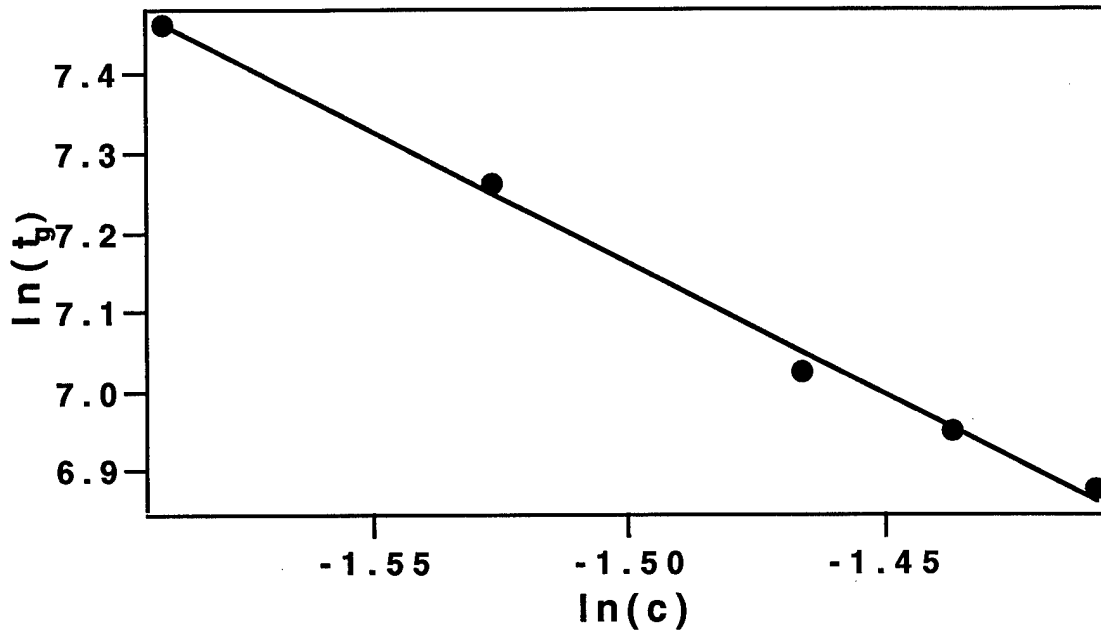


FIGURE 4. Gelation time for concentrated aqueous silica suspensions versus electrolyte concentration [“Slow gelation regime”].

forms are needed for realistic simulation of the gelation process in colloidal suspensions. As indicated above, the long-term goal of the project is to evaluate how gelation chemistry and kinetics influence ultimate gel properties and ceramic performance. This last will be investigated by performing yield stress measurements with the UDS.