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# STRUCTURE AND PROPERTIES OF RESORCINOL-FORMALDEHYDE GELS

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## ABSTRACT

The condensation polymerization of resorcinol and formaldehyde catalized by sodium carbonate produces a sol that aggregates to form a gel. Using viscometry the effect of temperature and catalyst concentration on the sol-gel transition was investigated. At a solids concentration of 3%, gelation occurred in 1500 minutes. The rate of increase in viscosity was a function of both catalyst concentration and temperature. The structure of the gels was studied by freeze-fracture TEM. In the sol phase the RF solutions contain particles of 5 to 20 nm diameter. After gelation the particles form a crosslinked network with a pore structure of 100 nm.

## INTRODUCTION

Foams made by supercritical drying of condensation polymerized resorcinol-formaldehyde (RF) gels are being developed for use as liquid DT wicks in direct-drive laser fusion targets. These organic aerogels were first described by Pekala[1]. The gel is formed by the aggregation of colloidal particles having a size range from 5 to 20 nm in diameter depending on catalyst (sodium carbonate) concentration[1,2,3]. After supercritical drying, the resulting foam has continuous porosity and a small pore size on the order of 100 nm. Our goals were to experimentally investigate the kinetics of gelation which has been theoretically modeled in the literature[4] and determine the relationship between gel and foam properties. The gels were studied by viscometry to understand the kinetics, and by scanning and transmission electron microscopy to determine the structure of the materials. The effects of two variable, catalyst concentration and temperature were explored. Catalyst concentration was shown[1,2] to control the particle size and the resultant foam density.

## EXPERIMENTAL

Solution mixtures of 3% resorcinol-formaldehyde with a varied molar ratio of resorcinol to catalyst in the range of R/C=50 to 400 were prepared. These solutions were transferred to sealed glass ampules to suppress oxidation of resorcinol monomer. The ampules were refrigerated for up to 2 months at 5 C until viscosity measurements were made. Generally, we obtained the same viscosity-cure time behavior indicating refrigeration did not interfere with the primary polymerization and aggregation mechanism to be studied. The RF solutions did, however, show a color change to a light brown showing some oxidation of the resorcinol. All solutions were run a minimum of two times to verify reproducibility.

The viscosity of the resorcinol-formaldehyde mixture was measured using a Rheometrics Fluids Spectrometer (RFS 8400). A couette viscometer was used with a 17 mm radius cup and a 16 mm radius bob that was 32 mm long. With this apparatus we were able to measure the dynamic viscosity in the range of 0.1 to 40,000 poise. All measurements were performed using oscillatory motion at a frequency of 1 radian per second with a 5% strain amplitude which prevented disruption of the gel structure. Gels were cured at a temperature of 60, 70, and 80 C. A 4 mm layer of mineral oil was used to prevent evaporation of water from the gel in the viscometer. The couette viscometer was coated with approximately a 2 μm layer of polystyrene (from a 1% methylene chloride solution) to eliminate possible metallic contamination form the tooling and to reduce cleaning problems.

Scanning and transmission electron microscopy was used to study the structure of the foam. An SEM with a field emission electron gun (Hitachi S-800) was used that allowed the use of low accelerating voltage to reduce beam damage problems. Foam samples were fractured at room temperature and then sputter coated with approximately 10 nm of platinum-carbon to reduce charging effects.

Freeze-fracture transmission electron microscopy (FFTEM) has been used to study the structure of dispersions[5,6], polymer gels[7,8,9] and colloids[10]. Our objective was to study the structure of RF solutions before and after gelation. In FFTEM the sample is frozen by a liquid propane jet (Gilkey-Staehelin, MF7200) at a rate of more than 10,000 K/s. Freezing at this rate produced an amorphous water phase and preserved the structure of the polymer gel. Fracturing was done at -120 C in a freeze etch system (Balzers, BAF400). After fracturing, the polymer phase was exposed by sublimation of some of the surface water by raising the temperature to -100 C for 15 minutes. The sample was rotary shadowed with platinum and carbon. The replica was cleaned on a solution of sodium hypochlorite and sodium hydroxide which removed all residual polymer.

## RESULTS AND DISCUSSION

Figure 1 displays the viscosity-cure time behavior of RF solution. The viscosity increased in two steps. In the first step the viscosity increased from a water-like viscosity of 0.01 poise to 100 poise in a time period of approximately 30 minutes. The rate of the initial rise in viscosity increased directly with temperature and catalyst concentration. Using titration to measure unreacted formaldehyde, Pekala has shown that the polymerization reaction has run to completion within 2 hours[2]. We attribute the initial increase in viscosity to polymerization and particle generation. After the initial rise in viscosity, the solution viscosity remains nearly constant for a period that depends on temperature. During this period, particles collide from Brownian motion and aggregate through the reaction of the surface groups. Approximately 1500 minutes later the viscosity rises from 100 poise to more that 10,000 poise. We have defined the second rise in viscosity where viscosity increases linearly with time as the gel time. The gel time was found to be a function of temperature as shown in Fig. 2. Increased temperature results in a shorter time to gelation as well as a higher rate of increase. We believe these phenomena are caused by faster particle aggregation because of greater Brownian motion at higher temperature.

Freeze-fracture transmission electron microscopy (FFTEM) was used to observe the morphology of particles in the reacting solution as well as in the final gel. FFTEM provided a way to observe, at high magnification, the process of aggregation of the polymer particles in the early stages of gelation. Fig. 3 compares the fracture morphology of a low viscosity RF solution having R/C=200 with its final gel. The low viscosity solution was prepared by reacting for 13 days at 22 C. The micrograph shows a structure composed of aggregated spherical particles approximately 20 nm in diameter. Prior to gelation, Fig. 3a, the aggregates are not interconnected but consist mostly of linear and branched chains of particles. After gelation, Fig. 3b, the particles become interconnected showing a structure composed of rings of particles with 20 to 50 particles per ring. The particle size and structure observed by FFTEM compare well with structures observed by SEM and TEM of supercritically dried foams. The SEM micrograph of a carbonized foam shown in Fig. 4 shows that the 20 nm particles have aggregated into a network with a structure having a "string-of-beads" morphology.

## CONCLUSIONS

The polycondensation of resorcinol with formaldehyde catalyzed by sodium carbonate was studied by viscometry and electron microscopy. Viscometry showed that the gelation proceeded in two steps: polymerization resulting in the formation of particles, followed by aggregation of the particles to form a stiff gel network. The initial particle formation step was a function of temperature. After a period of aggregation that resulted in no increase in viscosity, the viscosity of the gel increased linearly at a rate that depended on both temperature and catalyst concentration. Solutions with a lower R/C which produce smaller particles show a more rapid increase in viscosity.

Freeze-fracture TEM was used to study the structure of both the sol and the gel before drying and as a function of processing conditions. The solution is composed of a dispersion of 20 nm particles that have aggregated into strands of particles. After gelation, the strands interconnect to form a network having a string of beads morphology.

## ACKNOWLEDGMENT

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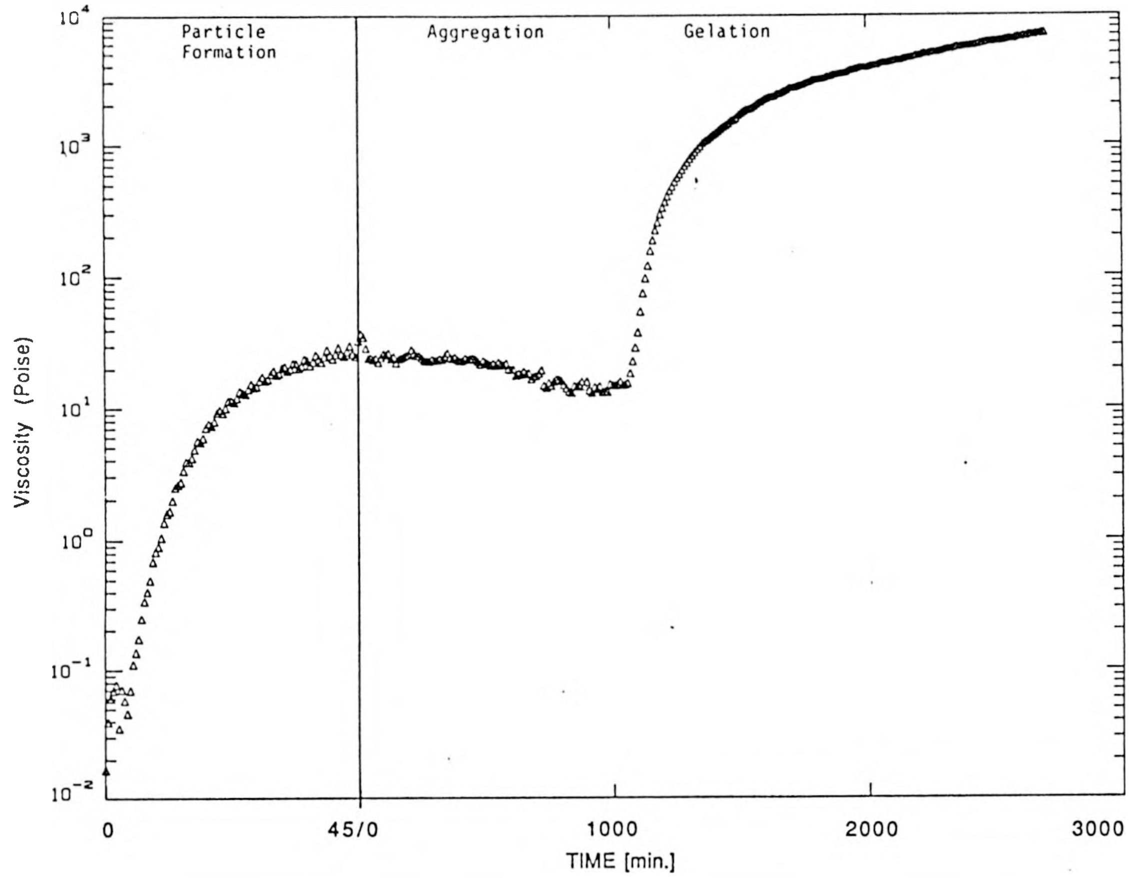


Figure 1. Viscometry of curing RF solutions show an initial increase from particle formation and a second increase form gelation.

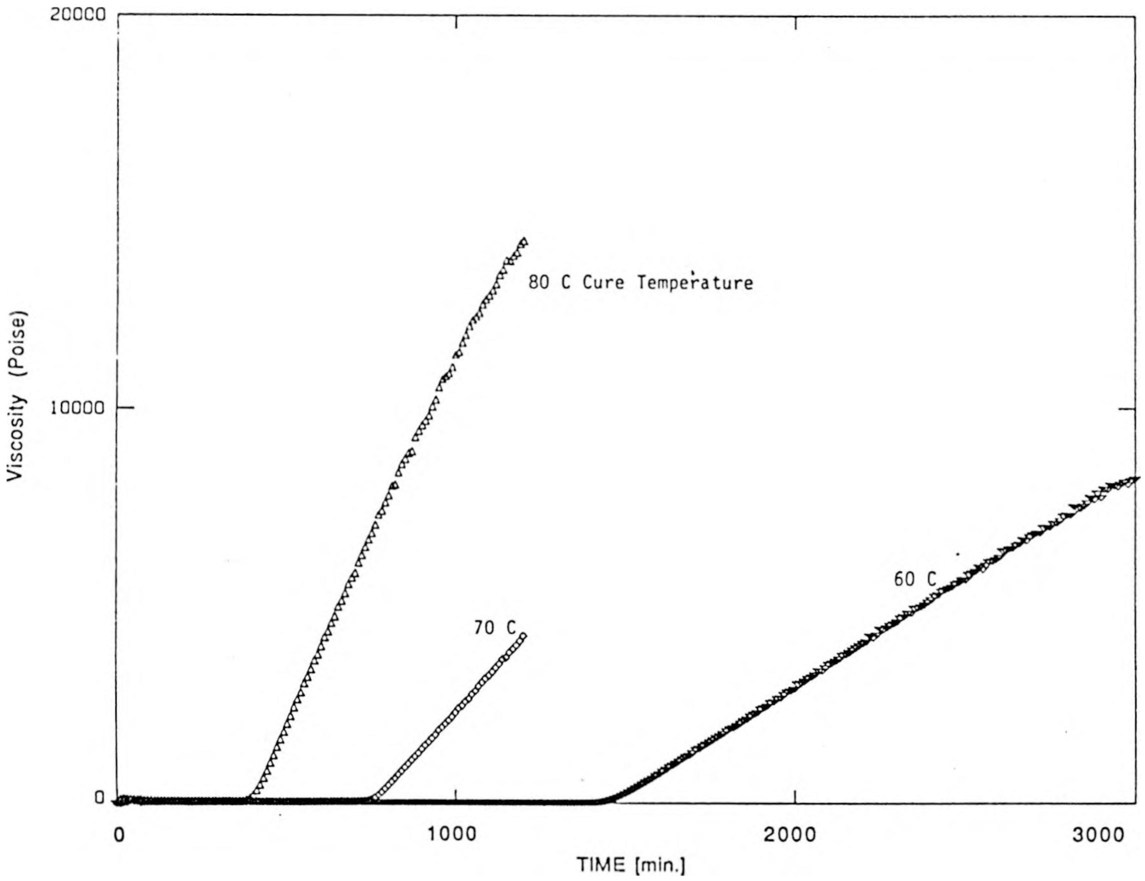
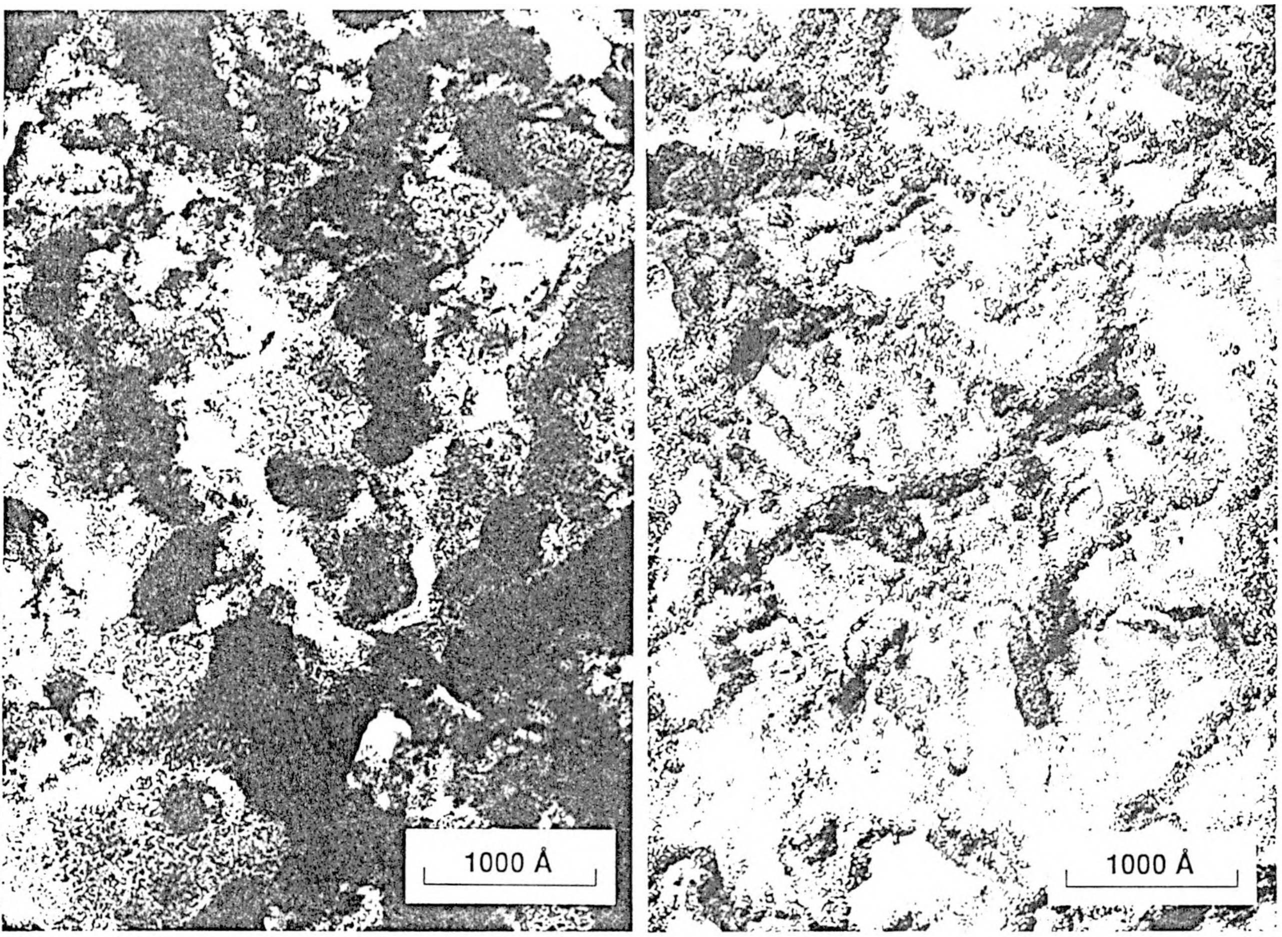


Figure 2. Increasing the cure temperature resulted in a faster gel time and a steeper increase in viscosity.



3a

3b

Figure 3. Freeze-fracture TEM shows that before gelation, 3a, the 20 nm particles are aggregated but not crosslinked. After gelation, 3b, a crosslinked network forms with 20 to 50 particles per ring.

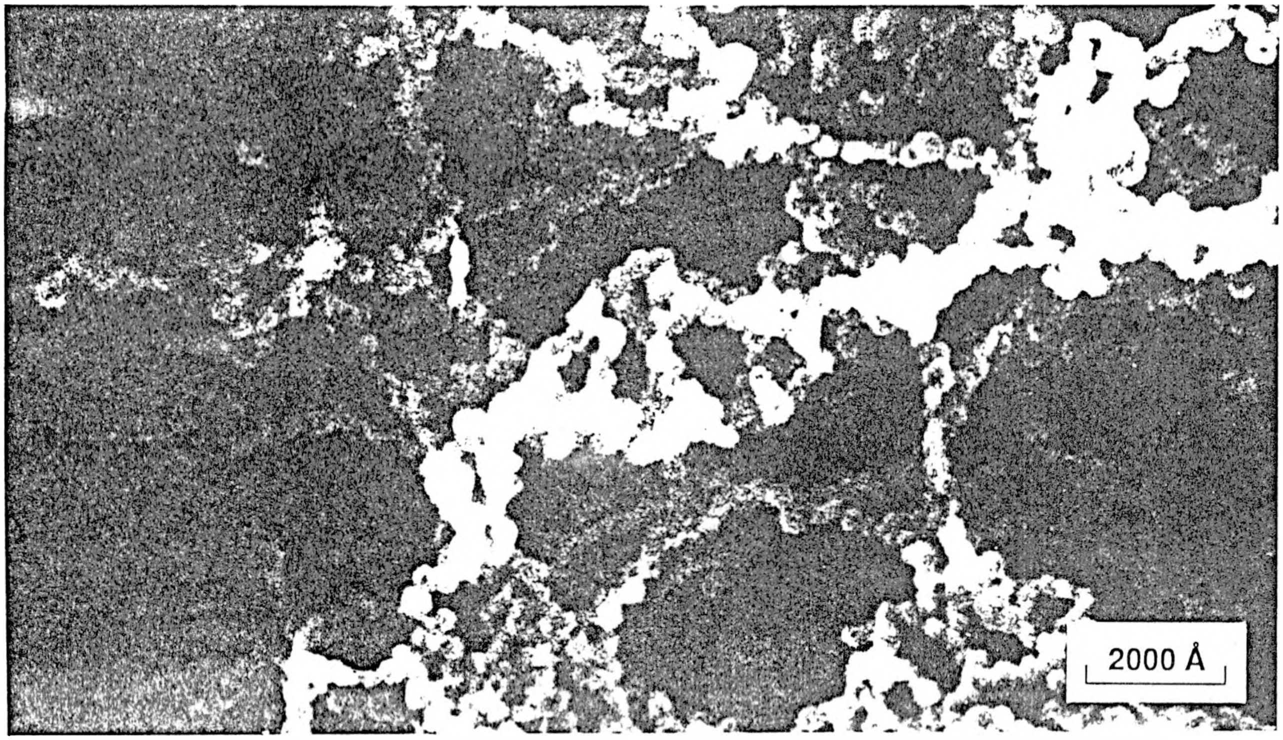


Figure 4. SEM of carbonized RF foam shows a string of beads morphology for the aggregated 20nm diameter particles.