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AEROGEL USING PHOTO-ACID GENERATORS FOR
INERTIAL CONFINEMENT FUSION EXPERIMENTS**

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NOVEMBER 2010



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Synthesis of Resorcinol Formaldehyde Aerogel Using Photo-Acid Generators for Inertial Confinement Fusion Experiments

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ABSTRACT

Traditionally, the synthesis of Resorcinol formaldehyde (R/F) aerogels consists of a 2-step (base/acid catalysis) polycondensation reaction. Since the acid catalyst in the reaction controls the gelation time, we are able to replace the acid catalyst with a non-ionic photo-acid generator decreasing the gelation time from hours, down to a few minutes at room temperature using a UV light source. Not only was the reaction rate fast, but the liquid precursor was stable for several hours prior to UV exposure. After drying, the resulting aerogel porosity was not changed significantly from the standard process. Scanning electron microscopy (SEM) confirms the internal structure of the aerogel was similar to the original and modified R/F pore structures. This paper will discuss the modifications made to the traditional R/F formulation, as well as the benefits of a fast gelation time for aerogel casting applications such as thin films, cylinders, and solid and hollow microspheres. The modified R/F formulation process also opens up the possibility of directly patterning aerogels into complex shapes on a surface using a photo-mask.

INTRODUCTION

Resorcinol formaldehyde aerogels are currently used in a variety of inertial confinement fusion (ICF) experiments in the form of solid and hollow spheres, cylinders, and thin films. These R/F aerogels are currently synthesized using the traditional 2-step polycondensation reaction devised by Pekala [1]. This 2-step polycondensation reaction consists of a base and acid catalysis step to form the R/F aerogel. The first step in the reaction was the base catalysis step which creates the hydroxymethyl aggregates; these aggregates react with one another to form the primary particles of R/F clusters. These particles then go through an acid catalysis step which bonds the particles together with methylene ether bridges to form the hydrogel. During the base catalysis step, small amounts of acid are generated [1] eventually leading to the gelation of the R/F. This reaction by itself would take significantly longer (hours to days) and not optimal for the experimental working time, necessitating additional acid. Heat was also used in both steps of this reaction to help speed up the process, allowing the gel to setup in the time frame for these experiments in a typical working day.

One of the main uses and designs for R/F aerogels in ICF experiments was in the form of hollow microspheres (spherical shells) as shown in figure 1, containing hydrogen isotope fuel. This was for future direct and indirect drive targets at the National Ignition Facility (NIF) and eventual use in an inertial fusion energy (IFE) power plant [2,3]. One of the issues with the R/F aerogel shells was meeting the wall uniformity specification. Investigations and process improvements at General Atomics (GA) have been made to the traditional R/F shell fabrication process first developed by Lambert *et al.* [4] to improve the yields of intact shells to 90% [5] and wall uniformity specification of 50% [6,7]. Though this yield may be acceptable for near term experiments, this yield was not acceptable for the HAPL energy plant design which required approximately a million shells a day.

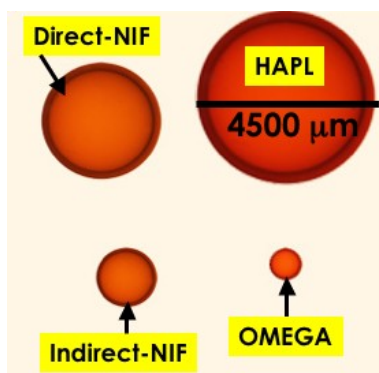


Figure 1. R/F capsules fabricated using the droplet generator method. Diameters of capsules: HAPL is 4500 μm , Direct-NIF is 3000 μm , Indirect-NIF is 1800 μm , and OMEGA is 880 μm .

The wall uniformity issue has led to the investigation of alternative methods such as dielectrophoresis (DEP) [8,9] to center and fabricate these R/F shells. DEP uses electric fields to move and center the shell while it was in its double emulsion form. The DEP process to center these shells was in development at the University of Rochester (U of R). U of R has developed a 20 MHz device and technique using DEP to center a double emulsion of water-oil-water [10,11]. The work done by Bei, *et al.* provided the parameters and requirements for the aerogel precursor solution to work in the device [10,11]. One of these parameters was the conductivity of the aerogel precursor solution needs to be in the 10^{-3} S/m range or lower; the other requirement was the precursor solution must gel at room temperature (RT) in 20 minutes or less. The shells must be cured at RT without heat because heating the DEP system will disrupt the electric field as well as damage the circuits used to create the electric field. Heat can also cause convection currents in the DEP centering device which can cause the double emulsion shell to not center. Based on these requirements, the current R/F synthesis technique was not compatible with the DEP device. This led to the investigation of other possibilities to synthesize the R/F aerogel and use a photo-acid generator (PAG) for the acid catalysis step.

PAG activates by exposure from UV light, producing an acid. If the acid produced by the PAG was strong enough, the gelation of R/F will occur in a matter of minutes as opposed to hours. The main concept for substituting the PAG into the R/F process was to control the time at which gelation of R/F occurs. Despite being able to successfully substitute the PAG for the acid catalysis step in the polycondensation reaction, problems arise in finding the right PAG to fit into the reaction and making the PAG soluble in the R/F precursor solution. This paper will discuss these issues and how insertion of the right PAG into the current R/F formulation creates an alternative method to synthesize the R/F aerogel.

EXPERIMENT

Selecting a photo-acid generator

The traditional R/F formulation for fabricating shells uses a precursor solution producing an aerogel with a density of 100 mg/cc, the density requirement for ICF experiments. This formulation was used to determine which PAG works the best for replacing benzoic acid in the acid catalysis step of the polycondensation reaction. A precursor solution consisting of resorcinol, formaldehyde, water, and a base catalyst (0.58 M sodium bicarbonate) are combined in a rotary

beaker and heated in a water bath at 70°C for 45 minutes. As the precursor solution heats, the base catalysis of the reaction occurs and R/F clusters begin to form in the solution. At the 45-minute mark, the precursor solution was removed from the water bath and chilled in an ice water bath for 10 minutes, allowing the reaction to slow down and reduce the acid formation in the solution.

After removing the precursor solution from the ice water bath, PAG was used as a substitute for benzoic acid. Several different PAGs were selected and tested based on the solubility in the precursor solution, reactivity to the precursor solution, and the wavelength at which the PAG activates. The precursor solution was divided into smaller, equal volumes and the desired PAG was added to the precursor solution. Since the volume of PAG being added to the precursor solution was small compared to the volume of diluted benzoic acid, the remaining volume of PAG was filled with water to match the volume total of benzoic acid and water in the traditional R/F formulation. To test the gelation of the R/F solution with the PAG, a droplet of R/F was suspended in a vial containing mineral oil, sorbitan monooleate (SPAN-80), and tetrachloroethylene (TCE). The mixing ratio of mineral oil to TCE suspended the R/F drops based on the density, and SPAN-80 was a surfactant added to prevent the R/F drops from agglomerating. Drops of the R/F solution with PAG were added to the vial and then exposed using a UV light source (Hg lamp, 100W Green Spot Model GS) as shown in figure 2. The PAG fitting the criteria of being soluble, non-reactive in R/F and a fast gelation time was the PAG used in synthesizing R/F for ICF experiments.

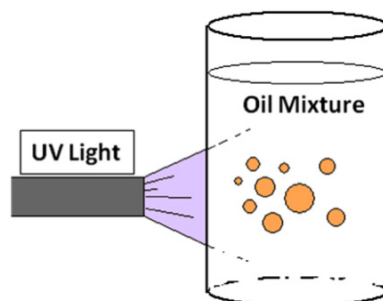


Figure 2. Droplets of R/F precursor with the PAG are suspended in an oil mixture and exposed to UV light. The suspension test was a quick way to determine the gelation time of R/F.

Fabricating R/F capsules with a photo-acid generator

The frequency of the field in a DEP device necessary to center a compound droplet depends on the conductivity of the droplet wall; the higher the conductivity, the higher the frequency required. Because of this, the conductivity of the precursor solution was critical for the solution to center using the DEP device. After selecting the PAG for the second step of the polycondensation reaction, the conductivity of the R/F solution was measured with a conductivity meter (VMR) to ensure the R/F was within the working range for the DEP device. If the R/F solution meets the conductivity requirements for the DEP device, it may be a possible candidate for the DEP centering device.

Another way to utilize the PAG in the R/F formulation was to apply it to the current R/F capsule fabrication process with the triple orifice droplet generator [4-7]. The droplet generator contains three orifices consisting of an inner oil (O1) line, the R/F precursor solution with PAG (W1) line, and an outer oil (O2) line. The O1 is an oil mixture containing mineral oil and TCE,

and the O2 is an oil mixture containing mineral oil, TCE, and SPAN-80. The O1 and W1 combine to form a double emulsion droplet, and suspended in the O2 throughout the gelation process. Density matching the R/F precursor solution with the O1 and O2 was necessary to keep the double emulsion suspended. As the double emulsion droplets of R/F and oil travel into a rotary beaker, the droplets are exposed to UV light for gelation as shown in figure 3.

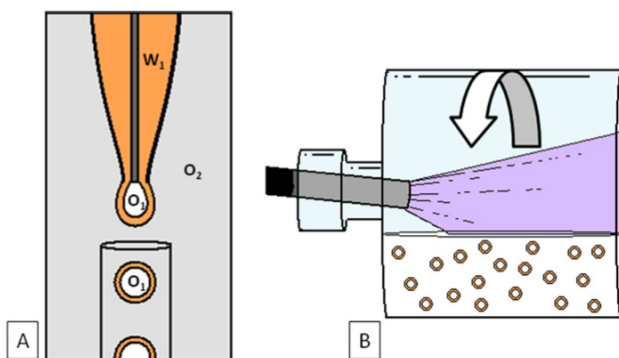


Figure 3. (a) Example of the encapsulation process of the double emulsion. W_1 is the R/F solution with PAG, O_1 is the inner oil mixture, and O_2 is the outer oil mixture. (b) The R/F capsules rotate in a rotary beaker while exposed to UV light.

After gelation of the double emulsion R/F droplets, the cured capsules undergo a post cure process to increase the cross-linking density of the R/F. The capsules were solvent exchanged into isopropanol to remove any water in the porous gel network and dried using a supercritical CO_2 drier to prevent shrinkage and cracking, preserving the low density structure of the resulting aerogel. After drying, the R/F capsules may then be handled to undergo characterization of the pore structure, surface roughness and wall uniformity.

DISCUSSION

Selection of PAG by droplet suspension test

Selecting the PAG to substitute the current acid catalyst (benzoic acid) in the traditional polycondensation reaction proved to be the most challenging aspect of the selection process. The first group of PAGs tested all contained the same triflate acid being formed when exposed to UV light. To verify if Pekala's 2-step polycondensation would work with the PAGs, trifluoromethanesulfonic acid (triflic acid) was initially used to prove gelation would occur. By substituting the triflic acid for the acid catalyst, the R/F precursor solution gelled instantaneously verifying the R/F will cure when the activated PAG forms triflic acid. The PAG, dimethyl 2,4-dihydroxyphenylsulfonium triflate (Oakwood Chemical), was selected because of its solubility in water. 0.00735M of PAG was dissolved in water to match the same molar concentration of benzoic acid used in traditional R/F formulation. The PAG solution was added to the R/F precursor solution after the base catalysis step. When adding the PAG solution to the R/F precursor solution, a white precipitate formed instantly at the bottom of the test vial. Since no UV light was exposed to activate the PAG, the white precipitate was not a result of R/F gelation. The R/F was exposed to UV light for 20 minutes, but the bulk solution remained liquid. Also, there was no change in pH after exposing to UV light. Glass tubes were placed in the vial to obtain R/F

samples for characterization. Even if the PAG did not activate to form an acid to speed up the gelation, the bulk R/F sample eventually gelled overnight (~12 hours) due to the small amount of acid being formed in the base catalysis step of the reaction. The R/F hydrogel in the tubes were removed and taken through the drying process to form the aerogel.

After drying the R/F samples, the aerogel was characterized by X-Ray Fluorescence (XRF) to analyze the composition of the white precipitate. Since the white precipitate cured in the R/F sample pieces, the white precipitate was analyzed on the XRF instrument. High XRF peaks corresponding to sulfur (or sulfur compounds) were present in the areas of the R/F where the white precipitate was present. Sulfur compounds in the aerogel are undesirable for use for ICF experiments because they increase the laser absorption of the aerogel wall of the capsule. According to Sigma-Aldrich, the PAG was an ionic compound containing a sulfonium ion. The addition of the PAG with the sulfonium ion created a side reaction with the R/F precursor solution forming the white precipitate. The results from this test suggest the PAG for the acid catalysis step of the polycondensation reaction would be better if it was a non-ionic compound.

The non-ionic PAG found to work with the R/F formulation was CGI 1907 (Ciba/BASF) shown in figure 4. Despite being a non-ionic, the PAG was insoluble in water but soluble in propylene glycol monomethyl ether acetate (PGMEA). The wavelength the PAG (200-325nm) activates within the range of the UV light source (300-480nm). When exposed to UV light, the PAG forms nonafluoro-n-butanesulfonic acid (nonafllic acid). A 0.2925 M solution of CGI1907 in PGEMA was prepared to use for PAG testing. A small volume of the PAG solution was exposed to UV light and the pH went from 6 to 3. Since the PAG solution was a strong acid when activated by UV light, 10 drops of the PAG solution were added to 15 mL of water. The water with drops from the PAG solution was added to 21 mL of R/F precursor solution. The volumes were based on the starting volume of R/F precursor solution after the base catalysis step, and the volume of diluted benzoic acid added to the precursor solution according to the traditional R/F formulation. To conduct the droplet suspension test, drops of the R/F solution containing the PAG were added to the oil mixture in a vial and exposed to UV light for 5 minutes. As the UV light shines on the R/F drops, the droplets begin to rise to the top of the oil mixture. When the UV light turns off, the R/F droplets return to the original height of suspension, indicating the relative density of the droplets are changing when the UV light was applied. The R/F droplets gelled after 5 minutes of exposure by UV light. The cured beads of R/F were then taken through the post-cure and drying process. Table 1 summarizes the PAGs used and the results from droplet suspension test.

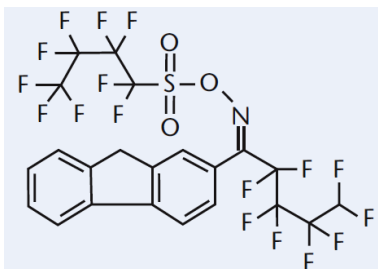


Figure 4. The chemical structure of the PAG, CGI 1907 (Ciba/BASF), used in the R/F formulation.

Table I. Summary of PAGs used in the droplet suspension test.

Photo-Acid Generator	Solvent	Acid Formation	Gelation Time	Comments
4-Phenylthiophenyl Diphenylsulfonium Triflate	Water	Trifluoromethanesulfonic Acid (Triflic Acid)	N/A	PAG does not dissolve in water
Dimethyl2,4-Dihydroxyphenylsulfonium Triflate	Water	Trifluoromethanesulfonic Acid (Triflic Acid)	~12 hrs	Forms white precipitate in side reaction with R/F, no change in pH with UV light exposure
IRGACURE121	PropyleneGlycol MonomethylEther Acetate (PGMEA)	p-TolueneSulfonic Acid	15 min	PAG re-crystallizes in R/F precursor solution; PAG particles on surface of R/F after drying
CGI1907	PropyleneGlycol Monomethyl Ether Acetate (PGMEA)	Nonafluoro-n-butanefulfonic Acid (Nonaflic Acid)	5 min	Fast gelation of R/F with the PAG

When removing the R/F beads from the drier, there appears to be a noticeable skin on the surface of the bead and an oily residue surrounding the bead as shown in figure 5. The skin surrounds the surface of the bead, and more apparent when examining the cross-section of the bead. It was possible the PAG in the R/F solution was only activated on the surface of the bead when exposed to UV light. Observing the R/F beads under the microscope, the skin on the beads appear to vary from bead to bead. While curing the R/F beads in the vial with the UV light, only certain areas of the bead were highly exposed to the UV light. Those areas were apparent when removing the R/F beads from the critical point drier. The skin on the beads was more noticeable on one side than the other due to overexposure of UV light. Even though the R/F beads have a skin on the surface, the process proves the PAG in the R/F solution will gel when exposed to UV light.

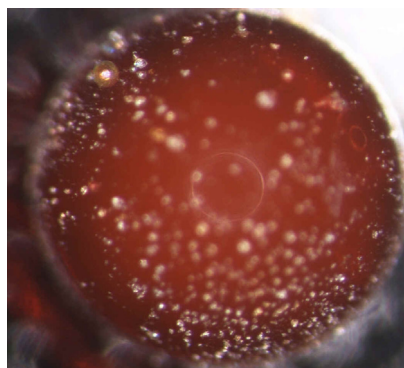


Figure 5. Image of 2 mm R/F bead taken after the drying process.

The pore structures were compared using the SEM images shown in figure 6. At 50,000X magnification, the SEM captures the pore structures of the traditional R/F formulation and the PAG R/F. According to the SEM images, the pore structures of the two R/F samples were visually similar. The pore structure for the PAG R/F looks slightly different because of the PAG molar solution made to conduct the droplet suspension test had a higher molar concentration than the benzoic acid used in the traditional R/F formulation. Using a strong acid for the acid catalysis step in the polycondensation reaction can change the pore structure of the foam. The higher

PAG molar solution was made to ensure gelation of R/F occurs as fast as possible when exposed to UV light.

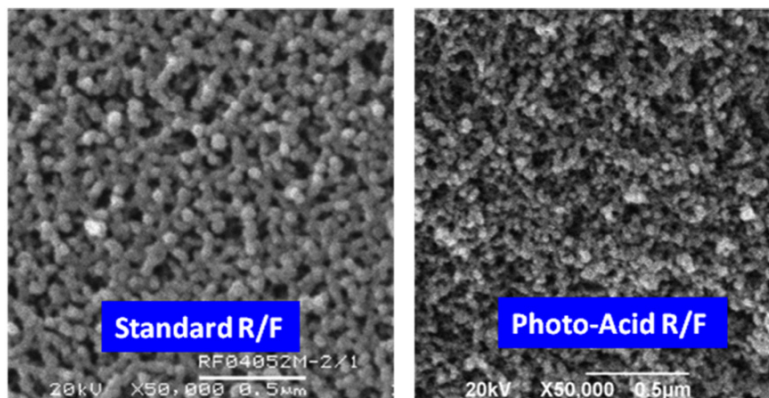


Figure 6. Side-by-side pore structure comparison of standard R/F and the PAG R/F via SEM.

Applying R/F with PAG to DEP

In order for the DEP device to be effective, the R/F solution containing the PAG must have a conductivity of 10^{-3} S/m or lower [10,11]. When testing the R/F solution, the conductivity was 4×10^{-2} S/m which was well out of the range the DEP device can be used. If the conductivity of the R/F was too high, the DEP was unable to center the double emulsion droplet. Despite the R/F with PAG having a high conductivity, it's not necessarily due to the addition of the PAG. The conductivity of the water, formaldehyde, and base catalyst (sodium bicarbonate) are measured individually before making the precursor solution. As it turned out, the high conductivity was a result of the base catalyst being added in the first step of the poly-condensation reaction [12]. Although the following R/F solution with PAG cannot be used in the DEP device due to the high conductivity, it may still be effective applying the solution to fabricating R/F capsules with the triple orifice droplet generator method.

The droplet generator method with PAG in R/F

Before using the droplet generator to fabricate R/F capsules, the R/F solution containing the PAG needs to be density matched [6,7]. A hurdle to overcome during density matching the solution was the change in density as the UV light was exposed to the R/F. During the droplet suspension test, it was found the drops of R/F with PAG would rise as the UV light shines on the drops. Since the drops rise with exposure to UV light, the R/F solution and oil mixture were density matched with the density of the oil being lighter than the density of the R/F.

After density matching, the R/F solution with PAG, outer oil mixture, and inner oil mixture were hooked up to the triple orifice droplet generator to create shells [4]. The uncured R/F shells rotate in the beaker and are exposed by UV light for 25 minutes. After exposing to UV light, the capsules were taken through the post-cure and drying process.

When the capsules come out of the drier, there appears to be a skin on the surface of the shell, but not as severe as the skin surrounding the entire surface of the beads fabricated during the droplet suspension test. Figure 7(a) and 7(b) were examples of a bead and capsule respectively, after the drying process. Since the R/F capsules were in constant motion in the

rotary beaker, the capsules have a limited amount of exposure to UV light. The UV light was constantly shining on the surface of the outer oil mixture, but only the R/F capsules moving near the top surface of the oil mixture are being exposed. Instead of the capsules being stationary like the beads, the capsules are in constant motion. Thus, the R/F capsules do not have the same type of exposure to UV light as the R/F beads and the skin on the capsule surface was not as extreme as the beads. In figure 8, the SEM image provides a closer look at the skin from a cross-section standpoint. Another hurdle of the R/F capsules being in constant motion was the inner surface of the capsule does not cure. The UV light source uses a light guide to emit UV light as a point source, focusing on a point rather than covering a broad area. By doing this, the UV light only activated the R/F capsules in the limited area the light was focused on. Ideally, the next step is to surround the rotary beaker containing the PAG R/F capsules with UV lamps to have a more uniform exposure of UV light. This may reduce the skin by not overexposing the PAG R/F with UV light and have greater contact with the UV light to gel the inner surface of the capsules.

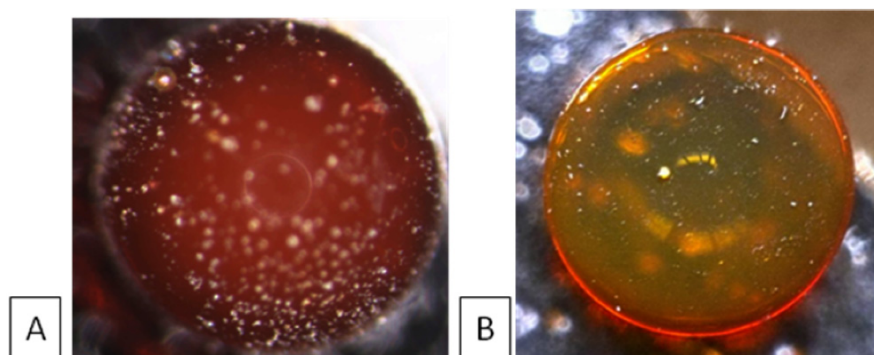


Figure 7. (a) 2mm R/F bead with the PAG CGI 1907. (b) 2mm R/F capsule with PAG CGI 1907.

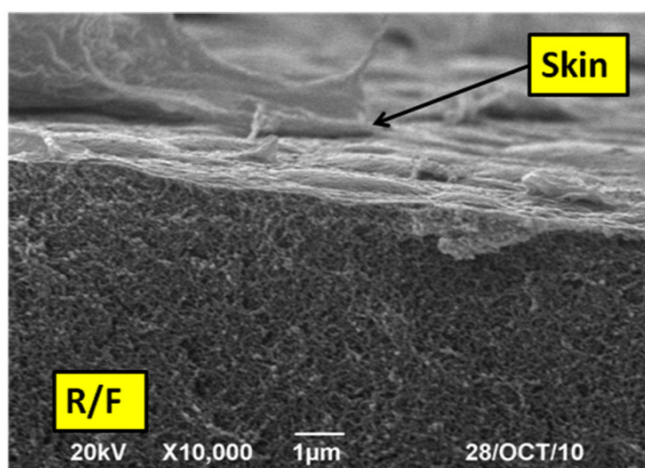


Figure 8. Cross-section of PAG R/F shell taken by the SEM.

CONCLUSION

The outlined experiments with the substitution of a PAG for benzoic acid as the catalyst in the 2-step polycondensation reaction show an alternative method to synthesizing R/F. Despite

the presence of skin on the R/F capsules and beads, the pore structure of the PAG R/F was very similar to the traditional R/F formulation. Despite being unable to utilize the DEP device due to the high conductivity from the base catalysis, the PAG R/F still applies to the triple orifice droplet generator method. Future work will include improvement on how the UV light exposes and contacts the R/F capsules during the curing process and optimizing the formulation and droplet generator process to produce usable shells for future ICF experiments using this alternative R/F synthesis.

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