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**SYNTHESIS OF RESORCINOL FORMALDEHYDE  
AEROGEL USING UV PHOTO-INITIATORS FOR  
INERTIAL CONFINEMENT FUSION EXPERIMENTS**

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## Synthesis of Resorcinol Formaldehyde Aerogel Using UV Photo-Initiators for Inertial Confinement Fusion Experiments

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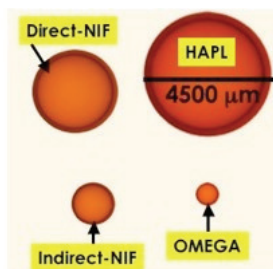
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### ABSTRACT

Resorcinol formaldehyde (R/F) aerogels have been used in a variety of laser targets for Inertial Confinement Fusion (ICF) experiments in the form of thin films, cast shapes such as cylinders and cubes, and hollow and solid microspheres. Besides ICF experiments, R/F aerogel can be used for capacitors, batteries, thermal insulation, absorption/filtration media, and chromatographic packing applications. Traditionally, R/F aerogel is synthesized using a 2-step (base/acid catalysis) polycondensation reaction. We have developed a novel process to synthesize the R/F aerogel using free radical UV initiator at room temperature in 10 minutes using a UV light source. This paper will review this process, which was developed to synthesize R/F aerogels using UV-free radical initiators. Scanning electron microscopy results will also be discussed to show that the aerogel pore structure is similar to traditional R/F aerogels. Fabrication of solid and hollow microspheres for ICF experiments using this R/F aerogel synthesis technique and the technique's limitations will also be discussed.

### INTRODUCTION

Resorcinol formaldehyde (R/F) aerogel is a low-density solid-state material derived from a gelation and liquid extraction process. This material can be used for capacitors, batteries, thermal insulation, absorption/filtration media, and chromatographic packing applications [1]. R/F aerogels have also been used in a variety of laser targets for Inertial Confinement Fusion (ICF) experiments in the form of thin films, cast shapes such as cylinders and cubes, and hollow and solid microspheres. Traditionally, these R/F aerogels are synthesized using a 2-step (base/acid catalysis) polycondensation reaction developed by Pekala *et al.* [2]. One of the main uses and designs for R/F in ICF experiments is in the form of hollow microspheres (shells) for future direct and indirect drive targets at the National Ignition Facility (NIF) and the High Average Power Laser (HAPL) programs pilot Inertial Fusion Energy (IFE) power plant [3,4]. These R/F foam shells are a scaled-up version of foam cryogenic targets currently used at the OMEGA facility at the University of Rochester Laboratory for Laser Energetics (LLE). Depending on the experimental design these spheres can have a diameter that can range from 900 to 4500  $\mu\text{m}$ . A picture showing the variety of R/F shell sizes and the design that they are used for is shown in figure 1. One of the issues with the R/F aerogel shells has been the yield that meets the wall uniformity specification. Ongoing investigations and process improvements at General Atomics (GA) have been made to the traditional R/F shell fabrication process that was first developed by Lambert *et al.* [5] to improve the yield of intact shells to 90% [6] and the shells that meet the wall uniformity specification to 50% [7,8]. Though this yield may be acceptable for near term experiments, this yield is not acceptable for the HAPL energy plant design that would require a million shells a day.



**Figure 1.** Shows the size difference between a variety of size ranges of R/F shells that can be fabricated. This can range from OMEGA (900  $\mu\text{m}$ ) to NIF (1500-3000  $\mu\text{m}$ ) to HAPL scale (4500  $\mu\text{m}$ ) R/F foam shell.

The wall uniformity issue has led to the investigation of alternative methods such as dielectrophoresis (DEP) [9,10] to center and fabricate these R/F shells. DEP uses electric fields to move and center the shell while it is in its double emulsion form. The University of Rochester (U of R) has developed a 20 MHz device and technique that uses DEP to center a double emulsion of water-oil-water [11,12]. The work done by Bei, *et al.* provided the parameters or requirements for the aerogel precursor solution that would allow it to work in the device [11,12]. One of these parameters is that the conductivity of the aerogel precursor solution needs to be in the  $10^{-3}$  S/m range or lower, the other requirement is that the precursor solution must gel at room temperature (RT) in 20 minutes or less. The reason why the shells must be cured at RT without heat is because heating the DEP system can 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 to become unstable and can result in the shell not centering. Based on these requirements our traditional R/F formulation used to fabricate shells cannot be used by the U of R DEP device due to its high conductivity ( $5 \times 10^{-2}$  S/m) and gelation time at RT (6-8 hours). This issue led to the investigation of modifying the R/F formulation to fit these parameters. This paper will discuss these modifications, which includes the use of UV free radical initiators to create a novel technique to synthesize the R/F aerogel. Characterization of the pore structure of these photo-initiated R/F aerogels will also be discussed to show that the aerogel pore structure is similar to traditional R/F aerogels.

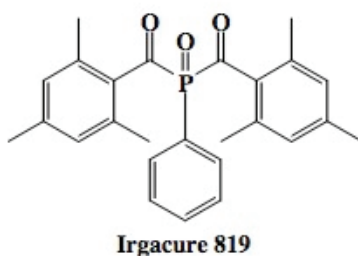
## EXPERIMENT

The R/F aerogel first developed by Pekala, *et al.*, is synthesized by using a two-step (base/acid catalysis) polycondensation reaction [2]. We will refer to this as the traditional formulation since it is the current formulation that is used to synthesize R/F aerogels. The traditional method begins with a precursor solution; the solution starts off with a base catalysis reaction using resorcinol, formaldehyde, water and a base (0.58 M sodium bicarbonate), which creates the hydroxymethyl aggregates, these aggregates react with one another to form the primary particle. These particles then go through an acid catalysis step (0.01 M benzoic acid), which brings these particles together by forming methylene ether bridges to form a hydrogel. Controlling solvent and precursor quantities can control the density of the aerogel; the target density for these experiments is 100 mg/cc. After curing the hydrogel, the gel is then solvent exchanged into isopropanol to remove any water in the porous gel network and supercritically

dried using a supercritical CO<sub>2</sub> drier to prevent shrinkage and cracking, preserving the low density structure of the resulting aerogel.

Before modifying the traditional reaction, conductivity measurements were taken of each component in the formulation using a conductivity meter. Conductivity of the precursor solution is critical for the solution to center using the DEP device because it determines the necessary frequency required by DEP to center the wall material of the spherical droplet. The current device developed at U of R has a maximum frequency of 20 MHz, which will work on solutions that have a conductivity reading in the range of 10<sup>-3</sup> S/m or less. A solution with a conductivity that is higher than this will not work on this device.

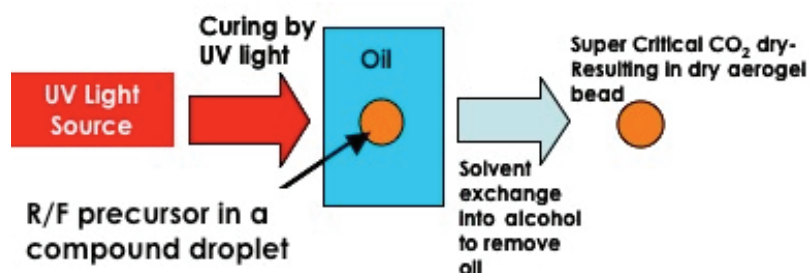
Modifications to the traditional formula were done in two ways, the first (Modification 1) was done by replacing the acid catalyst with a UV-free radical photo-initiator, the second modification (Modification 2) was to replacing both the acid and base catalyst with the a UV-free radical photo-initiator. Initiators screened for this work was two types of bisacylphosphine oxide (BAPO) under the trade name Irgacure 819 & 819DW (Ciba/BASF). Irgacure 819DW is a dispersion of BAPO in water while Irgacure 819 BAPO in a powder form. The structure of this BAPO initiator is shown in figure 2. To test if the solution would gel, a droplet of the precursor solution was placed into a vial filled with mineral oil and sorbitan monooleate (Span 80). A small amount of tetrachloroethylene (TCE) was added to keep the droplet suspended. The droplet was then exposed at RT to UV light using a Green Spot point source unit (American Ultraviolet); this unit uses a super-pressure 100-watt mercury lamp with peak intensity at 365 nm. If the solution gelled, the droplet now in a form of a solid hydrogel sphere or bead is then solvent exchanged with isopropyl alcohol (IPA) and dried using a supercritical CO<sub>2</sub> dryer. An illustration of the vial test process is shown in figure 3. Since the traditional method is driven by pH, the pH of the bulk solution was also monitored using a pH meter and was compared to the pH of an R/F precursor solution made using the traditional method. The aerogel was then measured for density gravimetrically and analyzed for its pore structure using a scanning electron microscope (SEM) and energy dispersive x-ray analysis (EDX), EDX was used to determine if the UV photo-initiators caused the R/F aerogel composition of carbon, hydrogen and oxygen to change.



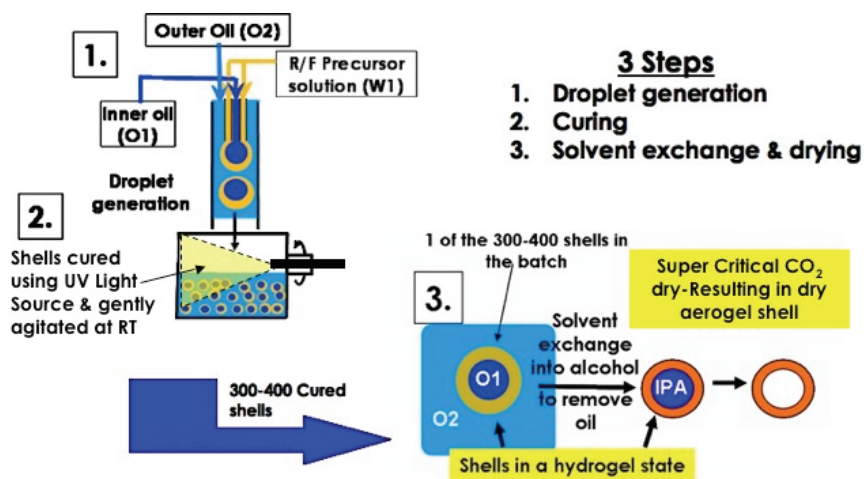
**Figure 2.** Chemical structure of the bisacylphosphine oxide (BAPO), which has the trade name Irgacure 819 (Ciba/BASF). This is the UV free-radical initiator that was used in these experiments.

If the modification produced a gel, the precursor solution was used to fabricate shells using our triple orifice droplet generator (DG) [5-8]. The DG method allows precise control of shell diameters and wall thickness, so that a large quantity of similar shells of a specified size can be made. This is similar to the methods described in reference 8; however, the only difference is that the shells are cured at RT using a UV light source. In this process, the DG creates a double

emulsion of an inner oil phase (O1), a R/F precursor solution (W1), and an outer oil phase (O2) [5-8]. The foam precursor is immiscible with the oil phases, allowing a liquid shell to form. The O1 solution is a mixture of mineral oil and tetrachloroethylene (TCE). The O2 is also comprised of a mixture of mineral oil and TCE with a small amount of sorbitan monooleate (Span 80). The Span 80 is the surfactant in the O2 that helps prevent the R/F shells from agglomerating. The shells and fluid are collected in the rotating flask and is exposed to UV light using the Green Spot until the shells are cured. After the shells are cured, they go through the same solvent exchange and drying process that the vial test beads go through. The shells are then tested in a similar method to the solid beads and are characterized by optical light microscopy for shell diameter and wall thickness. An illustration of this process is found in figure 4.



**Figure 3.** Illustration of the vial test used to check if the modification using UV-Free radical initiators can synthesize and form the R/F hydrogel.



**Figure 4.** Illustration of the DG Process that was used to fabricate R/F shells using UV-free radical initiators.

## RESULTS AND DISCUSSION

### Conductivity of the traditional R/F solution

Before modifying the traditional reaction, conductivity measurements were taken for each component in the formulation. The conductivity results shown in figure 5 indicate that the acid and base catalysts have the greatest influence on raising the conductivity of the R/F precursor solution. This is an issue because these are the catalysts that drive this reaction. These results



prompted us to explore other types of ways to synthesize R/F, which led to the investigation of using UV, free-radical initiators to replace the current catalyst. One issue with using a UV free-radical photo-initiated system is that it can only be used to gel or polymerize in the form of a thin film, but this works for our situation since our shells are a thin film in a spherical shape.

<b>R/F Formulation Components</b>	<b>Conductivity (S/M)</b>
DI Water	$6 \times 10^{-6}$
Formaldehyde	$3.3 \times 10^{-3}$
Carbonate Solution (Base)	$3.5 \times 10^{-1}$
Benzoic Acid Solution	$2.83 \times 10^{-2}$

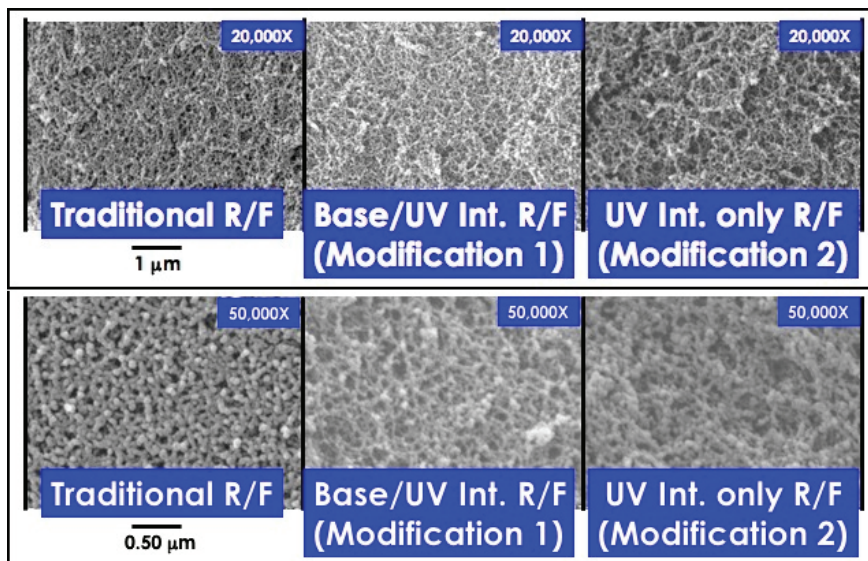
**Figure 5.** Conductivity results for each component of the traditional R/F formulation show that the acid and base catalysis are the components that increase the conductivity of the precursor solution.

Although the R/F precursor is a water based solution and most UV free-radical photo-initiators are not water soluble, we identified one that was semi water soluble, Irgacure 819DW, which was stated earlier as a dispersion of BAPO in water. Irgacure 819DW is a white milky liquid; we also examined regular Irgacure 819 which is in a BAPO in a solid powder form. In screening the initiators we added 0.10 wt% of the initiator to water. Neither initiator dissolved into water. Irgacure 819DW turned into small and large white droplets in the precursor solution which stayed at the bottom of the solution. The Irgacure 819 was dispersed in small particles due to its powder form. Over time the particles do sink, but if left suspended it is more evenly dispersed in the solution. The water/Irgacure 819 solution was then exposed to UV light using the Green Spot and the initiator particles dissolved in the water. As a result of this, Irgacure 819 was chosen as the initiator to use for these experiments.

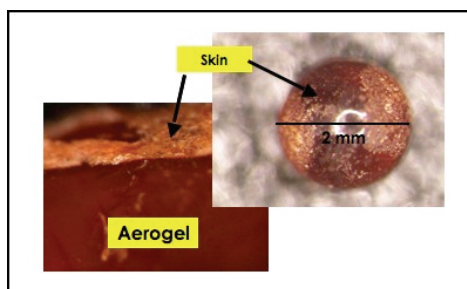
### **Replacing the acid catalyst with photo-initiator**

The first modification (Modification 1) was to begin with the traditional base catalysis step; this would start off the reaction and create the hydroxymethyl aggregates, which react with one another to form the primary particles to set up the hydrogel. After this step, 0.10 wt% of the initiator (Irgacure 819) was added to the precursor sol and mixed to suspend or dissolve the photoinitiator. To conduct the vial test, the precursor solution was added in the form of a compound droplet in a vial containing mineral oil and TCE. The results of the vial test show that the droplet of the Modification 1 solution when exposed by UV light activates the initiator to bring these primary particles together to form a hydrogel in 5 minutes. The hydrogel was then solvent exchanged and dried using a CPD. SEM images taken at 50,000 and 20,000X in figure 6 show that the pore structure is similar to R/F synthesized by the traditional method. The EDX analysis of the surface of the aerogel showed that the aerogel is still made up of carbon, hydrogen and oxygen. The density was also measured gravimetrically and is as calculated at 100 mg/cc. Optical images in figure 7 show that the surface has a rough skin, which could be an issue with the surface of the foam. Conductivity was also analyzed and the conductivity ( $3.3 \times 10^{-2}$  S/m) was still too high for the DEP device due to the carbonate in the precursor

solution. Despite the conductivity this showed that UV-free radical photoinitiators could be used to replace the acid catalyst and still form a R/F aerogel.



**Figure 6.** SEM images at 50,000 and 20,000X of traditional R/F, R/F made with replacing the acid catalyst with Photo-initiator (Modification 1) & R/F made with only UV initiator (Modification 2). Pore structure for all three look very similar with a pore size of less than 0.10  $\mu\text{m}$ .



**Figure 7.** Optical Image of a R/F aerogel bead fabricated by the vial test using Modification 1 (base/photo int.). The aerogel has a skin on the surface of the bead.

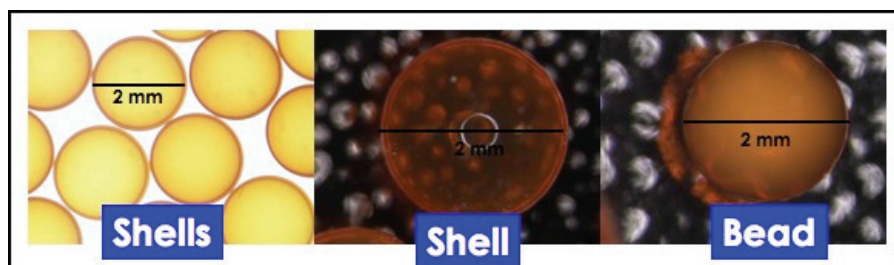
Because the modification formed a gel, it was then used to form shells in the DG. With the proper density matching Modification 1 R/F shells were successfully fabricated with a diameter of 2 mm and a shells wall of 100  $\mu\text{m}$ . Because shells were successfully fabricated this solution could still be used to fabricate shells despite not meeting the DEP requirements. Having the shells cure at RT has provided an advantage to the current DG process because we no longer have to density mismatch at a an elevated temperature of 70  $^{\circ}\text{C}$  which is more challenging. In addition, the faster cure time can be an advantage for production purposes. A summary of these modification experiments that displays the gelation time, conductivity and its pH change during the gelation process and how it compares to the traditional process is shown in figure 8.

The shells and beads fabricated on the DG showed little to no skin on the surface in contrast to the beads fabricated with the vial test (figure 9). This might suggest that the skin may be due to the way the shells and beads were exposed to the light, the DG shells are rotated and more

evenly exposed than the bead exposed in the vial test. SEM images of the pore structure of shells produced with the DG are also similar to the aerogels fabricated using the vial test and the traditional R/F. Density and EDX data were similar to the R/F bead fabricated with the vial test. The pH of the R/F solution was also monitored; the results show that once the photoinitiator is added and activated with this modification that the pH changes from 5 to 3. This suggests that an acid began forming once the free radicals were initiated by the reaction with water, or the hydroxyl groups on the primary particles. From this, one may suggest that the same reaction pathway is occurring for both processes driven by the changing of the pH. However, because the solution gels from a water-like liquid to a gel at RT much faster than the traditional method, which takes 20 minutes at 70°C, this suggests that something else is driving the reaction besides the formation of an acid.

Modification	pH During step 1	pH after step 2	pH During step 2	Conductivity (10 <sup>-3</sup> S/m)	Vial test - Gelation time (min) (at 70°C)	DG - Gelation time (min) (at 70°C)	Meets Requirements for DEP Centering
Standard	10	6	3	50	20	120	No
1	10	6	3	33	5	15	No
1- Low CO <sub>3</sub> <sup>2-</sup>	10	6	3	4.8	10	NA	Yes
2	6	3	3	3.0	10	20	Yes

**Figure 8.** Summary chart of the modifications that were investigated in finding a formula that would work in the DEP centering device, and to test if UV free radical initiators can be used to synthesize R/F aerogels.



**Figure 9.** Summary chart of the modifications that were investigated in finding a formula that would work in the DEP centering device, and to test if UV free radical initiators can be used to synthesize R/F aerogels.

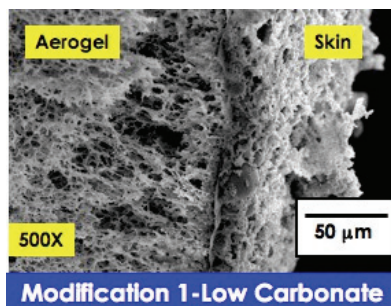
Because the conductivity for Modification 1 was too high due to the carbonate in the precursor solution, the carbonate was reduced in the solution so that the conductivity would be low enough to use in the DEP device. We will refer to this as Modification 1-low carbonate. In this modification the carbonate was reduced by 87%, which reduced the conductivity to 4.8x10<sup>-3</sup> S/m, which satisfies the DEP centering device requirement. The solution was tested for gelation using the vial test and the compound droplet gelled in 10 minutes at RT, which satisfies the gelation requirement. By satisfying these two requirements, this modification is a candidate for the DEP device. Similar to Modification 1, a skin is observed on the aerogel’s surface. One issue is that the pore structure is larger than our standard R/F aerogel. Large pore R/F aerogels are also observed in the traditional process when the carbonate is reduced [13,14]. A SEM image shown in figure 10 shows these large pores and the skin that forms on the surface of the

aerogel. Because large pore R/F can create issues in holding the fusion fuel for these experiments, it was not used to create a shell in the DG. But it can be used as a candidate for the DEP centering device as a proof of principle experiment.

### **Replacing the base and acid catalyst with photo-initiator**

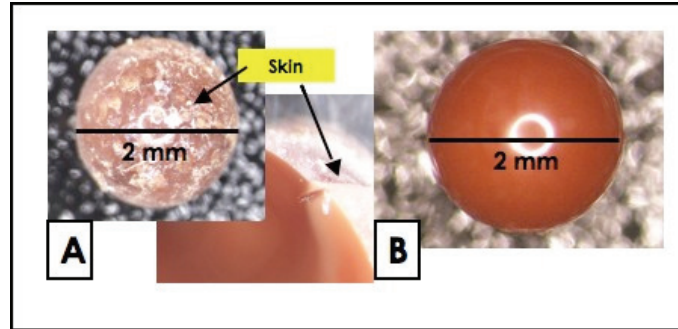
In Modification 2 both the base and acid catalyst were replaced with UV-free radical photo-initiator (Irgacure 819). The hope was to treat this still as a two step process in that a photo-initiator would be used like the base catalyst to form the hydroxymethyl aggregates which react with one another to form the primary particles. This would be followed with more initiators to bring these primary particles together to form the gel. In the first step the photo-initiator (0.10 wt%) did not fully dissolve into the sol when exposed to the UV light as the first modification. Because of this we added acetonitrile to the precursor solution to help dissolve the photo-initiator. The solution was then exposed with UV light for 15 minutes, the sol turned into a dark orange solution, without the acetonitrile the solution did not turn dark orange. The dark orange color is similar to the solution color of the traditional R/F solution, which suggests that the primary particles are forming. The pH of the solution at this stage went from 6 to 5. After this step, more initiator (0.10 wt%) was added to help bring these primary particles together to form the gel. The vial test results from Modification 2 gelled in 10 minutes at RT. The solution in the curing step also changed in pH from 5 to 3, similar to Modification 1. The measured conductivity of this R/F solution without the carbonate or acid was also measured to be an order of magnitude lower at  $3.3 \times 10^{-3}$  S/m, which meets the conductivity specification to be used in the DEP centering device. The gelation time of 10 minutes at RT also satisfies the second requirement for the DEP device, which makes this a candidate formulation.

Like the first modification the SEM images (figure 10) show that the pore structure is similar to the traditional R/F. Gravimetric density, EDX results are similar to Modification 1. Like the beads fabricated using Modification 1, the beads still have a skin on the surface; optical images are shown in figure 11(a). This solution was also used in the DG process but the acetonitrile in the precursor solution made the emulsion unstable causing the uncured shell to collapse into a bead before the shells cured. Like the first modification the beads that survived the DG process had little to no skin [figure 11(b)] when compared to the beads fabricated using the vial test. Despite these results, this shows the proof of principle that the R/F aerogel can be synthesized using only UV free radical initiators.



**Figure 10.** SEM Image of R/F aerogel fabricated using Modification1-low carbonate. Lowering the carbonate increases the pore size of the aerogel. This is also seen in the traditional process.





**Figure 11.** (a) Optical images of R/F aerogel beads made with the vial test using Modification 2 (UV int. only). Skin can be found on the surface of the bead. (b) Optical image of an R/F aerogel bead made with the DG using Modification 2 (UV int. only). Little to no skin can be found on the surface of the bead when compared to the vial test.

### **Limitations**

One limitation in using a UV free radical initiator is that it will only work for thin films and small areas and can not work for high aspect ratio parts or pieces. This creates a limit on what we can use this R/F aerogel for, which are for thin films and hollow or solid micro spheres. The thickest film that was successfully fabricated was a 1 mm thick film that was roughly 3X3 mm in area. Thicker films were not attempted but will be investigated in future experiments.

### **CONCLUSION**

These experiments helped produce a new novel technique synthesize R/F aerogel using UV-free radical initiators. These aerogels have a similar pore structure to the traditional R/F aerogel and can be cured at RT using a UV light source faster than the traditional method at RT and at 70°C. This was done by modifying the traditional formulation by either replacing the acid catalyst, or replacing both the acid and base catalyst. This work also produced formulations that are suitable to be used in the DEP centering device developed by U of R to center R/F shells, and these formulations also have the potential to be used in the traditional DG method to fabricate shells. Future work will include testing the potential formulations on the DEP centering device, improving the all UV photo-initiator formulation to survive the DG process and optimizing the formulation and DG process for both modifications.

### **REFERENCES**

1. R.B. Durairaj, "Resorcinol: Chemistry, Technology & Applications," Springer, Germany, (2005).
2. R.W. Pekala, et al., *J. Mater. Sci.* **24**, 3221 (1989).
3. J.D. Sethian, et al., *Nucl. Fusion* **43**, 1693 (2003).
4. J. Perkins, et al., HAPL Program Website:  
<http://aries.ucsd.edu/HAPL/DOCS/HAPLtargetSpecs.doc>
5. S.M. Lambert, et al., *J. Appl. Polym. Sci.* **65**, 2111 (1997).
6. A. Nikroo, et al., *Fusion Sci. Technol.* **45**, 84 (2004).
7. R.R. Paguio, et al., *Fusion Sci. Technol.* **51**, 682 (2007).

8. R.R. Paguio, *et al.*, accepted for publication in *Fusion Sci. Technol.* (2010).
9. H. Pohl, *Dielectrophoresis: The Behavior of Neutral Matter in Nonuniform Electric Fields*, Cambridge University Press, Cambridge (1978).
10. T. Jones, *Electromechanics of Particles*, Cambridge University press, New York (1995).
11. Z.-M. Bei, *et al.*, *Applied Physics Lett.* **93**, 184101 (2008).
12. Z.-M. Bei, *et al.*, *J. of Electrostatics* **67**, 173, (2009).
13. D.W. Schafer, *et al.*, *J. Non-Crst. Solids* **186**, 159 (1995).
14. C.A. Frederick, *et al.*, *Fusion Sci. Technol.* **49**, 657 (2006).