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FORMALDEHYDE AEROGELS FOR
FABRICATION OF HOLLOW SPHERES FOR
DIRECT DRIVE ICF EXPERIMENTS**

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Modifying the Pore Size of Resorcinol Formaldehyde Aerogels for Fabrication of Hollow Spheres for Direct Drive ICF Experiments*

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ABSTRACT

This work investigates an alternative way to modify the pore size of a 100 mg/cc resorcinol formaldehyde (R/F) aerogel without any significant change to the aerogel target density. This was successfully accomplished by an addition of hydrophilic polymer additive [Poly Vinyl Alcohol (PVA) or Poly Acrylic Acid (PAA)] to the R/F precursor solution which acts as an impurity in the reaction. The polymer can modify the cross linking or aggregation of the primary particles which can change the structure formation of the aerogel, thus changing the pore size. This paper will discuss this process modification and the fabrication of hollow, large pore R/F aerogel spheres that are used for direct drive inertial confinement fusion (ICF) cryogenic ice layering experiments at the University of Rochester Laboratory for Laser Energetics (LLE). The aerogels were characterized using scanning electron microscopy (SEM), nitrogen gas adsorption, and ultra small angle x-ray scattering (USAXS).

INTRODUCTION

Hollow spherical targets (shells) of resorcinol formaldehyde (R/F) aerogel are employed in direct drive inertial confinement fusion (ICF) experiments on the OMEGA facility at the University of Rochester Laboratory for Laser Energetics (LLE) and will be used in future experiments on the National Ignition Facility (NIF). The shells needed for OMEGA experiments have diameters of ~800–900 μm which are scaled down versions of the targets that are required for high gain wetted foam direct drive ignition designs on NIF [1]. The required wall thickness for these shells is 40–60 μm with an aerogel density of 100 mg/cc. The standard R/F aerogel used in these experiments is transparent due to its small pores of <100 nm [figure 1(a)]. We refer to this as the standard method (STD method). Because the aerogel is an open cell porous material, the aerogel shell by itself cannot hold the required fill gas (D_2 or DT). For these wetted cryogenic aerogel shells to hold a fill gas, a pinhole free permeation barrier is over-coated around them.

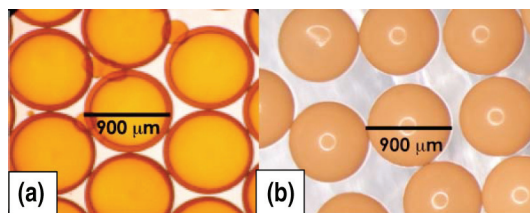


Figure 1. (a) Standard R/F shells. These shells are transparent. (b) Large pore R/F shells made with the PA Method (using PVA). These shells are not transparent and are opaque.

Cryogenic ice layering experiments at LLE using hollow R/F shells have shown advantages of larger pore aerogels compared the pore sizes of the standard R/F formulation. This led to the request for hollow R/F shells with larger pores [figure 1(b)] for cryogenic ice layering experi-

ments. Previous work on modifying the pore size of the R/F aerogel to produce hollow shells was done by decreasing the base catalyst to resorcinol ratio, creating a large pore R/F aerogel ($\sim >0.5 \mu\text{m}$) through reaction limited aggregation [2,3]. We will refer this as the low-catalyst method (LC method). A drawback to the LC method is that the final density was 30% lower than the calculated density [3]. The density reduction is due to less catalyst in the base catalysis part of this two-step polycondensation reaction, which forms less hydroxymethyl adducts due to unreacted monomer in the reaction. Another drawback was the instability of the precursor solution at room temperature (RT) and the gelation time at (the STD R/F precursor solution's gelation temperature of) 70°C . This caused the solution to gel faster (10 min. at 70°C and 2–3 hours at RT) than the standard R/F solution (15–18 min. at 70°C and >12 hours at RT). Previous work showed that the gelation time of the precursor solution was key in producing hollow R/F shells, the process required the solution to be stable at room temperature for >6 hours, allowing consistent behavior of the R/F precursor throughout the encapsulation run and the solution should gel within a 15–18 minute time frame at the precursor's gelation temperature [4–6]. This issue for gelling the solution in the required time was done by lowering the gelation temperature to 65°C , which allowed the fabrication of a large yield ($\sim 90\%$) of intact shells [3]. But despite being able to produce shells, because the LC precursor solution was unstable at RT, it reduced the time period that we were able to produce shells. Instead of being able to produce shells in a 4–5 hour period after adding the acid, it was now reduced to less than an hour, this time constraint made the fabrication of these shells more difficult than using the standard fabrication process. These results lead us to investigate alternative ways to produce larger pore R/F aerogel that would be more compatible with our current shell fabrication process. This work investigates an alternative way to modify the pore size of the R/F aerogel without any significant change to the aerogel target density. This was successfully accomplished by an addition of hydrophilic polymer additive [Poly Vinyl Alcohol (PVA) or Poly Acrylic Acid (PAA)] to the R/F precursor solution which acts as an impurity in the reaction. We will refer to this as the polymer addition method (PA method). The polymer impurity can modify the cross linking and aggregation of the primary particles which can change the formation of the aerogel, thus changing the pore size. This modification successfully increases the pore size of the R/F aerogel with little or no change to the precursor's gelation time when compared to the standard process which made it possible to use the same shell fabrication process used for standard pore size R/F aerogel shells [4–6]. This paper will discuss the process modifications and the fabrication of hollow, large pore R/F aerogel shells. The resulting aerogels were characterized for aerogel structure using scanning electron microscopy (SEM), nitrogen gas adsorption, and ultra small angle x-ray scattering (USAXS).

EXPERIMENTAL

The R/F aerogel, first developed by Pekala, et al., begins with a precursor solution that forms into an aerogel by a polycondensation reaction using a two-step (base/acid catalysis) polycondensation reaction shown in figure 2 [7]. The precursor 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 which 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 to form the gel by forming methylene ether bridges. Controlling solvent and precursor quantities can control the density of the aerogel. The gel is then solvent exchanged into isopropanol to remove any water in the porous gel network and supercritically dried using a

supercritical CO₂ drier to prevent shrinkage and cracking, preserving the low density structure of

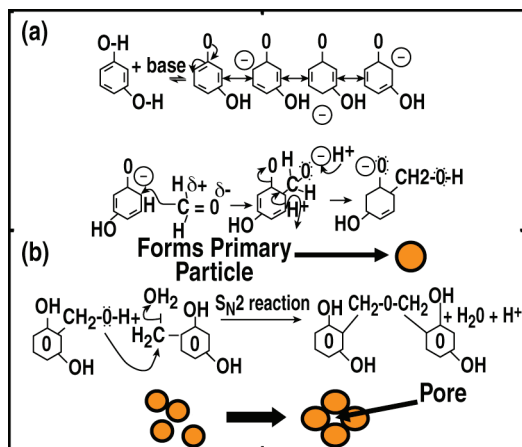


Figure 2. R/F aerogels are fabricated by a 2 step polycondensation reaction. (a) (Base Catalysis) Resorcinol ring is activated which allows the formaldehyde to attack the resorcinol, which results in the formation of hydroxyl methyl adducts (primary particle). (b) (Acid Catalysis) In this step the primary particles react and aggregate with one another forming methylene ether bridges and leads to the gelation of the R/F precursor solution. The aggregation of the primary particles can influence the pores of the aerogel.

the resulting aerogel.

Drawbacks from the previous work using the LC method [3] lead us to investigate alternative ways to produce a large pore R/F aerogel that would be more compatible with our current shell fabrication process. The alternative method used to increase the pore sizes in the aerogel was to add known impurities of a hydrophilic polymer to the water based R/F precursor solution (PA Method); the polymer impurity in the solution would modify the aggregation of the primary particles and increase the pore size. Impurities in polymer synthesis reactions are known to cause changes to the structure of the polymer. By not reducing the base catalyst, it leads to a larger pore aerogel with a final density that was closer to its calculated density. PVA and PAA (Polyscience, Inc.) were the hydrophilic polymers that were used for this modification. We dissolved the polymer (0.1 wt% PAA or 0.3 wt% PVA) into the water portion of the R/F precursor solution formulation. Bulk samples of these aerogels were produced using the PA, STD and LC method and were analyzed for its pores and aerogel structure.

These techniques include scanning electron microscopy (SEM), nitrogen gas absorption (Micromeritics ASAP 2020), and USAXS using the Advanced Photon Source (APS) USAXS instrument at the Argonne National Laboratory. USAXS is a nondestructive measurement technique in which the intensity of elastically scattered x-rays at small and ultra-small angles is recorded after they pass through the sample. As the x-rays scatter from inhomogeneities within a sample they deliver structural information about the sample [8]. The APS USAXS instrument is sensitive to more than three decades (1 nm to above 1 μ m) of microstructural feature sizes, measured in a single 15-min long scan [8]. The data was reduced using the Indra software package [9].

The fabrication of hollow R/F shells was first developed by Lambert, et al. [10], whose work was extended at General Atomics to develop a process to fabricate a high yield (~90%) of OMEGA sized shells, and the process has been described in previous papers [3–6,10]. The R/F shells are fabricated using a triple orifice droplet generator (DG), 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. One key factor in fabricating a high yield of R/F shells from the previous work is that the gelation time of the precursor solution must be stable at room temperature for >6 hours, allowing consistent behavior of the R/F precursor throughout the encapsulation run and the solution should gel within a 15–18 minute time frame at the precursor's gelation temperature [4–6]. In our standard baseline process, the DG creates a double emulsion of an inner oil (O1),

R/F precursor solution (W1), and an outer oil (O2). When introduced into the droplet generator the precursor solution has just started the acid catalysis step in the R/F gelation process [6,7]. 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 placed in a water bath at the precursors curing temperature to complete the gelation. The cured shells are solvent exchanged with isopropyl alcohol (IPA) and dried using a supercritical CO₂ dryer.

The dried shells are over-coated with a pinhole free gas permeation barrier. Glow discharge polymer (GDP) was chosen as the permeation barrier for these shells. GDP was overcoated on the shell by chemical vapor deposition (CVD) [5,11]. The barrier is tested for gas retention by permeation filling the shells with argon (Ar), and analyzing the shells by x-ray fluorescence (XRF), by following the decay of Ar signal in the shells as a function of time [3,5].

RESULTS AND DISCUSSION

Prior to shell fabrication, bulk samples of the aerogel were produced to observe the precursor's stability, gelation time, and optical clarity. The standard pore R/F used is transparent, a modification that resulted in larger pores would produce a more opaque aerogel due to the increased amount of light scattering caused by the larger pores near the wavelength of visible light. This was also observed in our initial large pore modification experiments [3] and was observed in our new modifications using the PA method.

Bulk R/F aerogel samples were analyzed using nitrogen absorption which provided the BET (Brunauer, Emmett and Teller method) [12] surface area of these aerogels. The results in figure 3 show that the modified R/F aerogels have a smaller surface area than the standard R/F aerogel.

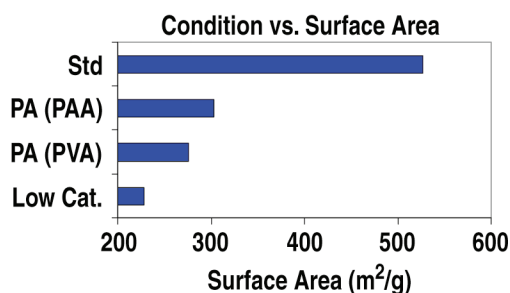


Figure 3. Nitrogen absorption data of the large pore and standard small pore R/F foams. The surface area increases as pore diameter decreases due to the increase in volume occupied by larger sized pores.

Since the surface area decreases as the pore diameter increases (due to the increase in volume occupied by larger sized pores), this is a good indication that the pore size of the foam increased.

These bulk samples were then imaged using SEM. The results of the SEM images from these samples are shown in figure 4(a–d). The SEM images show that these modifications have changed the structure when compared to the standard transparent aerogel [figure 4(a)], and these modifications have larger voids or pores. The LC method [figure 4(b)] shows that the primary particles are larger than the other 3 samples analyzed, and that this increase leads to the increase in the pore size of the aerogel. The PA method samples are both similar to each other in respect to primary particle size, but we do see a web-like structure in the SEM images [figure 4(c,d)] which shows larger voids or pores than the standard R/F sample.

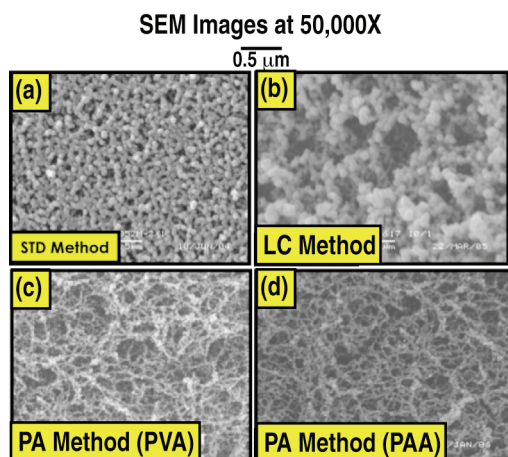


Figure 4. SEM images of the R/F aerogels made with different methods, showing the structure and pores of the aerogel. The LC, and PA methods show that it has larger pores and a different structure than the R/F fabricated using the standard method.

After acquiring this data, these bulk R/F samples were analyzed for their structure using the APS USAXS instrument. Because the aerogel is $\sim 5\%$ solid material and is mostly empty space, most of the scattering is from the solid material and not the voids. Usually, for more common low porosity materials, the scattering is dominated by the scattering from the voids, in which case the structure of the pores can be analyzed. However, in the present case of high-porosity materials, the USAXS provides information on the solid structure of the aerogel, at least at high- Q data. At small Q values, where the microstructure is probed on large length scales, the dominating inhomogeneities in this material can be caused by a large void or structure. As this microstructure is quite complex, we must use a combination of both the USAXS and the SEM to deduce the changes to the overall aerogel structure by processing modifications.

A plot showing the scattered intensity vs. scattering vector (Q) from the USAXS is shown in figure 5. Information on the particle size and structure can be determined from this scattering data using, for example, an Unified fit method by Beaucage, et al. [13]. To analyze the structural features of these aerogels using this method we need to analyze the Guinier areas, also referred to as knees, which supply information on the size of scatter using radius of gyration (R_g)

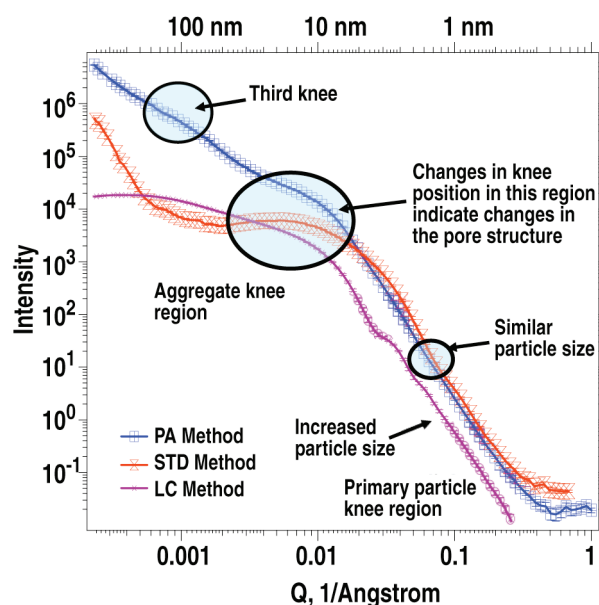


Figure 5. Reduced data of the USAXS scans of these R/F aerogels made with different methods. This data along with the SEM data can provide a way to interpret the pore and structure change of the R/F aerogel due to the various process changes using the LC and PA method.

approximation. The R_g values are related to various sizes of the primary particles as well as any inhomogeneities in the aerogel. These knees are followed, at higher Q values, by regions of power-law exponential decay, which can either provide information about the shape and structural arrangement of the scattering features or their specific surface area, depending on the power law slope. The detailed analysis of the exponential decay areas has not been attempted in this short work, but may be addressed in future publications.

Significant change in scattering curve, figure 5, for LC method produced sample indicates major change in the structure of this sample as compared with STD and PA method produced samples. The shift in the knee between 0.01 and $0.06 \text{ \AA}^{-1}$ to smaller Q values indicates that LC manufactured sample has larger primary particles size than STD sample, in agreement with SEM data. PA method produced sample exhibits more complex behavior, which is discussed later, but the high Q data agreement between STD and PA curves indicates, that the primary particles for the STD and PA method are similar, also in agreement with the SEM data. Unique to USAXS and very valuable information about the structures shows in the second knee region at Q values below $0.001 \text{ \AA}^{-1}$ where the aggregation of the primary particles manifests itself. In this region the three methods of sample manufacturing results in significantly different curves indicating major structural differences in these modified aerogels.

For STD method, the presence of low- Q power law uptick is sign of presence of large-scale inhomogeneities slightly outside the USAXS range. Therefore we can estimate that these inhomogeneities are at least 5 microns large. These cannot be further characterized by the USAXS method as not enough information is available in the USAXS data. One possible explanation is, that these inhomogeneities are from large voids in the aerogel, but data from several SEM images taken of the STD aerogel reveal no indications of any $5 \text{ \mu m}$ and larger voids. A second explanation is, that the scattering causing this uptick at low Q is from a larger structure in the aerogel. Even if there are voids of this magnitude in the aerogel, the sensitivity of USAXS at this size range is high and therefore the volume of the voids would be small enough to not have a significant effect on the aerogel's transparency. For the LC method, it appears that the particle sizes and aggregation of the particles are similar to the standard R/F. However, the fact that the intensity curve does not deviate up at low Q values (as for the other samples) is indication that large-size pores are either not present or, since these are observed on SEM, that these are significantly out of the range for the USAXS instrument. Therefore we can estimate, that these large pores would have to be at least 10 micrometers in size or larger. The PA method R/F shows steadily increasing power law towards low Q and even a third knee that is not seen in the other R/F samples. This indicates that there may be size range of large inhomogeneities in the aerogel, in the size range of submicron to over micron, that are formed during the aggregation of the primary particles which forms the web like voids or pores that we see in the SEM data. The polymer acts as a template for the web like structure that is seen in the SEM. The particles aggregate around the polymer and once the polymer is removed with the water during the solvent exchanged step, the aerogel is left with these web like voids which creates the larger pores that are seen. This has been seen in earlier work by Han et al., where they used silica particles as a template which was etched out of the R/F to form a larger pore foam [14].

One reason for investigating other ways to change the pore size of the R/F is to find a method that would make the precursor solution compatible to the shell fabrication process. Previous work using the LC method resulted in precursor solution that was unstable at RT and gelled faster than out STD R/F solution. This lead to modifications to the fabrication process to produce shells [3], but the instability of the solution leads to inconsistencies and issues in the

fabrication process. The PA method produced a R/F precursor sol that behaved similar to the standard R/F solution. The gelation time at 70°C and the stability of the PA precursor was identical to the STD R/F precursor solution. Because of this we were able to use the same standard R/F shell fabrication process to produce these shells, which resulted in a similar yield (~90%) to our standard R/F shells, and we did not have the time constraints that we did using the LC method. Similar results were shown for both PVA and PAA polymer additions, but because we were able to filter the precursor solution easier using the PVA modification due to its lower MW (25 K for PVA, and 1 M for PAA), PVA became the polymer of choice. Another improvement to using the PA method was that the measured density was equal to its calculated density of 100 mg/cc, this was not the case with the LC method. The density of the aerogel was done gravimetrically.

After the shells were made the shells were overcoated with a GDP by CVD in order to hold a fill gas such as D₂ or DT for ice layering experiments. A 4–5 µm thick overcoating of GDP is needed to produce a gas retentive coating. For these larger pore foams a much thicker overcoat is needed, which is another indication that the pore structure has changed. In order for these large pore R/F shells to hold a fill gas, a 10–12 µm coating was required. The shells that held gas were sent for LLE for ice layering experiments.

CONCLUSION

We were able to successfully develop a method to produce a larger pore R/F aerogel that was more compatible with our established fabrication process to produce the hollow R/F spheres. This new method also did not have the dramatic density change that was seen using the previous large pore fabrication method. Besides looking at methods that were used to analyze the structural modifications to the R/F with the previous work, we also investigated USAXS as another method to analyze these structural changes. The large pore R/F aerogel shells fabricated with this method were overcoated with a gas retentive overcoat using a GDP and sent to LLE for ice layering experiments.

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