

Encapsulation of low density plastic foam materials for the fast ignition realization experiment (FIREX) –control of microstructure and density–

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Abstract. Development of foam capsule fabrication for cryogenically cooled fuel targets is overviewed in the present paper. The fabrication development was initiated as a part of the Fast Ignition Realization Experiment (FIREX) Project at the ILE, Osaka University in the way of bilateral collaboration between Osaka University and National Institute for Fusion Science (NIFS). A foam cryogenic target was designed where low-density foam shells with a conical light guide will be cooled down to the cryogenic temperature and will be fueled through a narrow pipe. The required diameter and thickness of the capsule are 500 μm and 20 μm , respectively. The material should be low-density plastics foam. We have prepared such capsules using 1) mixtureing a new material of (phloroglucinolcarboxylic acid)/formalin (PF) linear polymer to control kinematic viscosity of the precursor, 2) phase-transfer-catalyzed gelation process to keep density matching of three phases of the emulsion. 3) non-volatile silicone oil as outer oil of emulsion in order to prevent hazard halogenated hydrocarbon and flammable mineral oil. The obtained foam capsule had fine structure of 180 nm (outer surface) to 220 nm (inner surface) and uniform thickness reaching to resolution limit of optical analysis ($\sim 0.5 \mu\text{m}$). A small hole was made before the solvent exchange and the drying process to prevent distortion due to volume changes. The density of dried foam was 0.29 g/cm^3 . After attaching the petawatt laser guiding cone and fueling glass tube, poly([2,2]paracyclophane) was coated on the foam surface and supplied for a fueling test of cryogenic hydrogen.

Generally, lower density is from larger pore, then precise control of thickness and its encapsulation becomes more difficult. We have clarified the relation between pore size and preparation conditions using several precursor materials, and revealed how to control pore size of low density foams, where the solvent affinity for the polymer chain plays fundamental role. By a gelation of PF solution and extraction to remove the organic solvent, PF aerogel was obtained to be 145 mg/cm^3 . The pore size of the PF aerogel was less than 100 nm while that of previous RF/PF mixture was 200-500 nm. The SEM showed that PF had particle-like foam structure while RF had fibrous-like foam structure.

1. Introduction

The fast ignition concept is one of the most attractive paths to inertial fusion energy [1, 2]. After the invention of the hollow cone/shell target geometry [3], the heating of the deuterated hydrocarbon plasma was demonstrated upto nearly 1 keV temperature using Gekko XII and petawatt laser facilities at Osaka University [4-6]. Fuel target technology is a key issue in fast ignition research [7, 8]. To achieve the breakeven gain, the fast ignition realization experiment (FIREX) was designed and started with construction of a 5 PW laser in the phase of FIREX-1 [9, 10] and cryogenic DT fuel target.

In the design of target for FIREX-1, the diameter of the fuel shell is $\sim 500 \mu\text{m}$, which is similar to that for a central ignition target for Gekko XII. To fabricate a uniform, non-spherical solid-deuterium-tritium layer, a low-density foam supports liquid or solid fuel ($\sim 20 \mu\text{m}$ thick) and the shell is covered with a thin (1 – 5 μm) plastic layer.

There are several kinds of foam materials for IFE targets [15], and resorcinol-formalin (RF) is one of the leading materials due to its high transparency in a visible region, which allows routine characterization of shells using well-developed optical techniques including interferometry. The details of RF shell fabrication were reported by a U.S. group [16 - 19], where an RF polymer solution and density-matched oil formed an emulsion through a triple orifice droplet generator. The emulsion was converted into hollow foam shells. The density range was $100 \sim 200 \text{ mg/cm}^3$,

and the thickness was 30 ~ 60 μm . A fuel barrier membrane was coated with the so-called glow discharge polymer (GDP) by their method, where the smoothness of the surface depended on the surface roughness of RF foam structure [18].

Recently, we found a new gelation method using a phase-transfer catalyst [20], which can exhibit a constant density of the oil and water phases and gave highly concentric shell, because the phase-transfer catalyst activated the gelation reaction at room temperature and kept density matching between O and W phases. New linear polymer prepared from phloroglucinolcarboxylic acid and formalin (PF) was also invented in order to form thinner shells through an increase of viscosity of W phase [21]. To prevent hazard halogenated hydrocarbon and flammable mineral oil, a mixture of silicone oil (SO) was chosen as outer oil [22]. Here, we overview RF-PF capsule fabrication using integrated technique of the O/W/SO emulsion process, the phase-transfer catalyst, and RF-PF gel, and show the fabrication with gold cone and fueling glass tube.

Generally, lower density is from larger pore, then precise control of thickness and its encapsulation becomes more difficult [15]. We have clarified the relation between pore size and preparation conditions using several precursor materials, and revealed how to control pore size of low density foams, where the solvent affinity for the polymer chain plays fundamental role [23, 24]. By a gelation of PF solution and extraction to remove the organic solvent, PF aerogel was obtained [25]. The pore size of the PF aerogel was less than 100 nm while that of previous RF/PF mixture was 200-500 nm. The reason also can be explained the solvent affinity for the polymer chain.

2. Phase-transfer catalyst for gelation reaction

The hollow spherical gel was obtained by combining several techniques. The key process is density matching emulsion technique. In the case of spherical gel formation from RF emulsion, the gelation catalyst was activated by heating, previously. In the process, because of the density-mismatch of W and O during the reaction as shown in Fig. 1, we have not obtained highly spherical capsule.

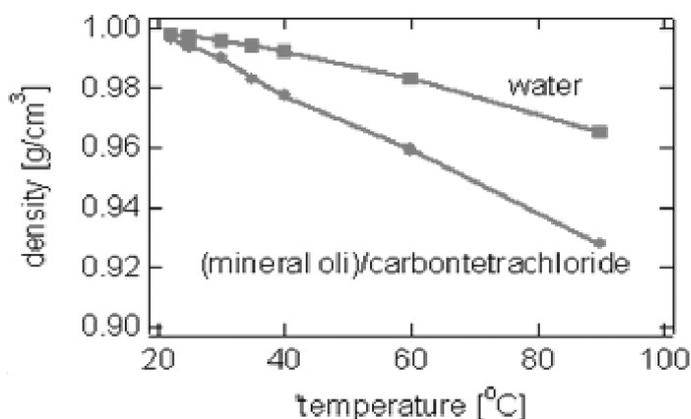


FIG. 1. Density of the emulsion component depending on temperature. While the densities of the RF aqueous solution and oil (mineral oil and carbon tetrachloride) were well matched at the room temperature, density mismatch happens during heating due to different slope depending on temperature.

Figure 1 shows the densities of water and oil [(mineral oil)_{wt}/carbontetrachloride_{wt}= 12 g/7 g] depending on the temperature. The densities of water and oil were well matched at room temperature. Both densities decrease with high temperature, and the slope of the oil is higher than that of the water. But the matching was lost at high temperature, and the droplets gradually sank to the bottom. The heating activation has a dilemma of the optimization of catalyst concentration [19]. While the pore sizes and density were improved by increasing the catalyst concentration, the systems gelation time had been decreased. The faster gel time led to poor nonconcentricity for

shells. Recently, we found that a phase-transfer catalysis polymerization of RF emulsion [20], where the catalyst was dissolved into the outer oil phase. The crosslinking, i.e., the gelation reaction starts gradually from the outer surface of RF solution. The gelation time was controlled by changing the concentration. For example, in the case of acetic acid, the time was 20 ~ 90 minutes for the concentration of 3.9 % ~ 0.07 %, respectively. The pore size was decreased with the catalyst concentration from 460 to 130 nm.

3. Mixing of a linear phenol/formalin polymer (phloroglucinolcarboxylic acid and formaldehyde) and non-volatile silicone oil as outer oil of emulsion

Next, we adopted silicone oil (SO) as an outer oil to alter toxic halogenated hydrocarbon and flammable mineral oil [21]. The adoption of silicone oil has another merit to circumvent exact density matching because of its very low volatility. Using the compound emulsion, O/W/SO, the highly concentric RF capsule was obtained by optimizing fabrication conditions such as rotation speed of the round drum, how long it kept, when it started etc.

In spite of these optimizations of manufacturing process, the minimum thickness of RF foam was 100 μm , which was 5 times as thick as the specification of the FIREX fuel target. In order to obtain thinner thickness, viscous water phase (RF solution) should be applied. Figure 2 shows the relation between minimum wall thickness (S) versus the high kinematic viscosity (ν) of water phase using a droplet generator. The higher ν value gave the thinner S values. Higher ν value of water phase than $9 \times 10^{-5} \text{ m}^2/\text{s}$ induced instability to form emulsion using the droplet generator [26], therefore the exact thickness values were not measured. Although we have tried to use high- ν RF solution, such viscous RF solution easily changed to gel due to crosslinking reaction in highly concentrated RF polymer. To circumvent the crosslinking of RF solution, we have adopted linear copolymer composed of phloroglucinolcarboxylic acid and formaldehyde (PF) (chemical structure is shown in Fig. 6) [22], where phloroglucinolcarboxylic acid has only two reactive positions (hydrogen) in an aromatic ring, therefore it is impossible to induce crosslinking reaction.

The viscosity of this mixture solution was chosen to be $9 \times 10^{-5} \text{ m}^2/\text{s}$, which corresponds to 20 μm wall the W phase as seen in Fig. 2.

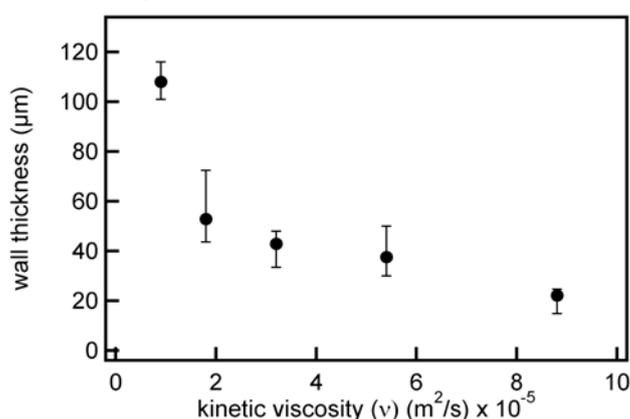


FIG. 2. Wall thickness of W phase in $O_1/W/O_2$ compound emulsion depending on viscosity of W phase. O_1 ; 1-methylnaphthalene, W; PVA solution, O_2 ; mixture of that polydimethylsiloxane (KF-96-10cSt, Shin-etsu Chemical) and poly(1,1,1-trifluoropropylmethylsiloxane) (density = $1.018 \text{ g}/\text{cm}^3$, $\nu = 4.5 \times 10^{-5} \text{ m}^2/\text{s}$).

By using the RF-PF mixture solution and the triple-orifice droplet generator, actually emulsions with 20 μm thickness and 500 μm diameter were prepared. Thirty droplets were transferred to a drum flask (700 mL) with the silicone mixture and 0.39 % acetic acid as a phase-transfer catalyst, and then rotated and its speed increased to 95 rpm within 5 minutes. Five minutes later the rotation speed was increased to 120 rpm. The rotation speed was maintained for 1 minute, and

then reduced to 95 rpm, which was maintained for 50 minutes.

After gelation, the capsule was exchanged with 2-propanol/water mixture 4 times whose ratio was gradually increased linearly to neat 2-propanol. Then the 2-propanol gel was dried by supercritical-fluid-CO₂ extraction. But, when a gelated capsule was dipped into 10 wt% aqueous 2-propanol, the wall of the capsule was dimpled. Therefore, part of the capsule surface was spaced using a drill, and then the O_i of the capsule was removed by hexane, and then water in the capsule was exchanged with 2-propanol. Figure 3a shows a hydrogel with a small hole. There existed small expansion (0.5 % in diameter) during exchange in to 2-propanol. After the 2-propanol was removed by extraction using supercritical CO₂, 2% shrinkage happened in diameter. Figure 3b shows the image of dried capsule after laser machining of a hole with 300 μm diameter to attach cone guide.

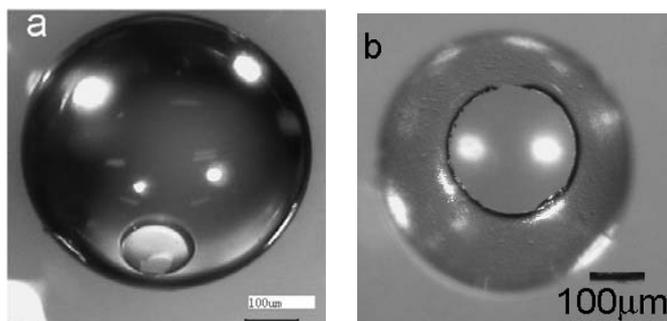


FIG. 3. Optical image of RF-PF shell, a) hydrogel with a small hole to prevent distortion and before exchange of solvent, b) dried and after laser machining of a hole for attaching gold cone.

The density of the foam was estimated for a hollow shell. The foam shell diameter, the thickness were 514 μm and 8 μm, respectively, and its volume was $6.5 \times 10^{-6} \text{ cm}^3$. The density was calculated to be 0.29 g/cm^3 from the volume and the mass (1.9 μg). Due to shrinkage, all of the balls had a higher density than the gel concentration. The oxygen content of RF-PF was similar to that of RF, while phloroglucinolcarboxylic acid has more oxygen than of resorcinol.

4. Pore Size control of low density materials

We have investigated the relation between pore size and preparation conditions using several precursor materials, and revealed how to control pore size of low density foams, where the solvent affinity for the polymer chain plays fundamental role. Here, we describe a typical example in the case of polystyrene based epoxy group opening reactions. A monomer, 4-vinylphenyloxirane (**M1**) and styrene were copolymerized using azo-bis(isobutyronitrile) (AIBN) as an initiator. The solutions of the obtained polystyrene-based copolymers in 4-chlorotoluene were gelled by the addition of a cationic initiator, which caused cross-linking via ring-opening polymerization of the pendant cyclic moieties. SEM images of the dried gel show various foam structures (Fig. 4). The formation mechanism of the micro- and nano-structure was explained from the view point of the affinity of the monomer unit and the solvent as shown in Fig. 5. The homopolymer of 4-vinylphenyloxirane showed a “no-void” structure and its average particle size was 50 nm, which was the finest and most uniform structure in the series. There is the possibility that no-void without microphase separation and smaller particle skeleton would be formed by using a low-affinity solvent to the polymer as shown in Fig. 5 [24].

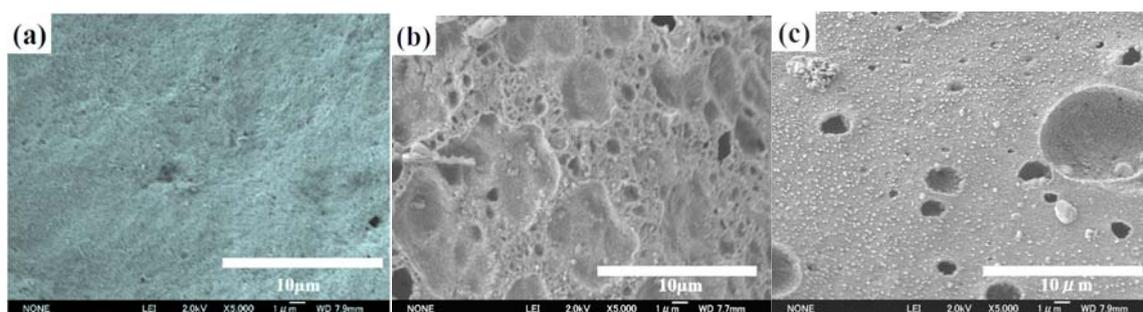


FIG. 4. SEM image of the dried gel surface obtained from (a) 0.07wt% solution of homopolymer of **MI**, (b), (c) 0.07wt% solution of copolymer of styrene (32%, 44%) and **MI** (68 %, 56%), respectively. The homopolymer was formed no void ($\sim\mu\text{m}$) structure, while voids appeared on the surface of copolymers. In case of (b) and (c), distorted and spherical voids were observed, respectively.

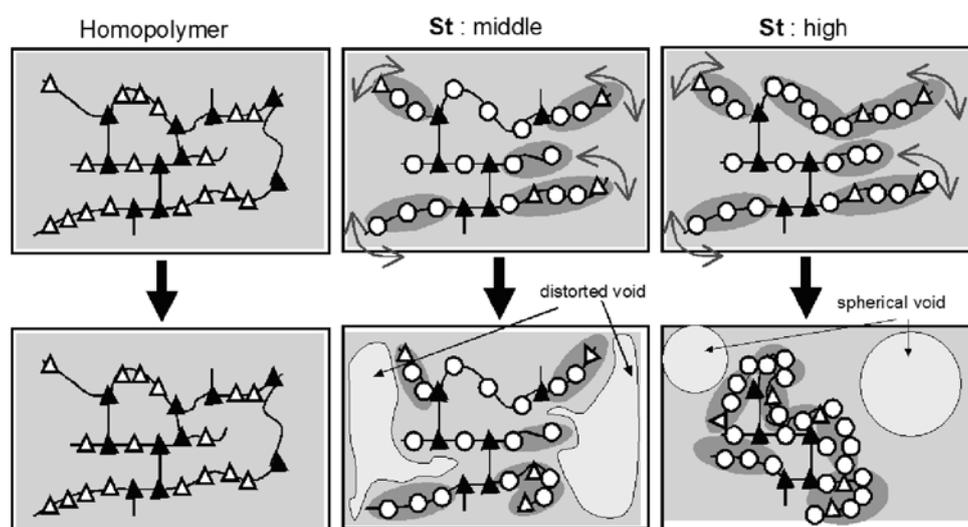


FIG. 5. Schematic view of microphase separation process. As seen in Figure 4, the differences of morphology appearing on the surface depend on the molar rate of **MI**. The solvent affinity of the chain depends on the monomer unit. Styrene and unreacted **MI** would exhibit high solvent affinity and mobility. Branched part of **MI** should have low mobility.

5. Encapsulation of decananometer-pore foam

Recently we found decananometer-pore foam which is one-order smaller than the previous one. Capsules with a thin aerogel shell were prepared by the $O_0/W/O_1$ emulsion process. (Phloroglucinol carboxylic acid)/formaldehyde (PF) was used as the water phase (W) solution to form the shell of the capsule [25]. PF is a linear polymer prepared from phloroglucinol carboxylic acid. The viscosity of the PF solution can reach a high level of $9 \times 10^{-5} \text{ m}^2/\text{s}$ without gelation while resorcinol/formaldehyde (RF) gels at $\sim 3\text{-}4 \times 10^{-5} \text{ m}^2/\text{s}$. Using the viscous PF solution, capsules with a $17 \mu\text{m}$ shell were fabricated. This thickness also satisfies the specification of (FIREX-I). When PF gel was extracted to remove the organic solvent, shrinkage of 9% occurred. The final density of the PF aerogel was $145 \text{ mg}/\text{cm}^3$. The pore size of the PF aerogel was less than 100 nm while that of RF was $200\text{-}500 \text{ nm}$. The SEM showed that PF had particle-like foam structure while RF had fibrous-like foam structure. The present difference also can be explained the affinity of the solvent to polymer skeleton.

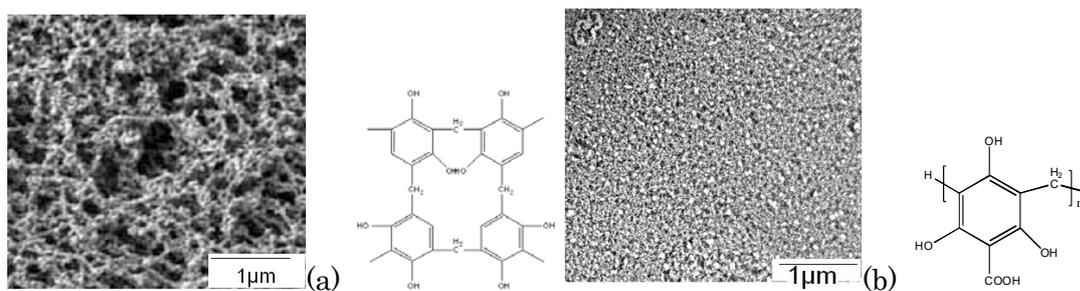


FIG. 6 SEM images and chemical formula: (a) RF aerogel (b) PF aerogel. The pore sizes of RF and PF aerogel are 200-500 nm, <100 nm, respectively.

6. Target assembly

The detailed characterization was done for gelled capsule (before exchanging solvent to 2-propanol) as shown in Fig. 7, because dried capsule has a hole drilled in order to remove 1-methylnaphthalene as described before. The analysis process is shown in elsewhere [21]. In this case of Figure 7, the outer diameter was 504 μm and the out of roundness in mode 2 was 2 μm. Distance between inner and outer surfaces shows wall thickness of the gel. The average thickness of the RF-PF capsule was 19 μm and the mode 2 non-uniformity was 1.5 μm. The present optical image has resolution of the same order of the mode 2 of the thickness. A large hole for increasing gold cone was fabricated using laser machining. Figure 3b is the picture after the laser process [27]. Finally the capsule was assembled with a gold cone as for guiding of the heating laser, and a glass capillary for liquid hydrogen fueling as shown in Figure 8. Preliminary fueling tests are on going [28].

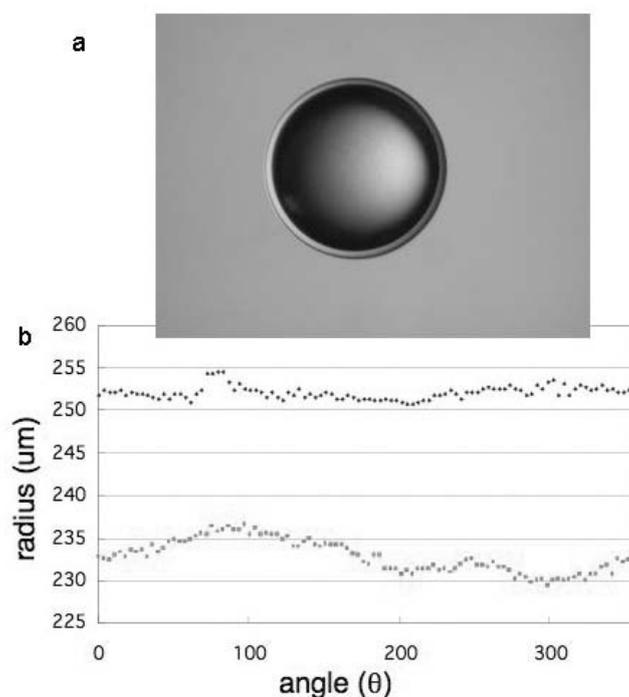


FIG. 7. (a) Optical image of a gelled capsule and (b) radius depending on angle by an image analysis

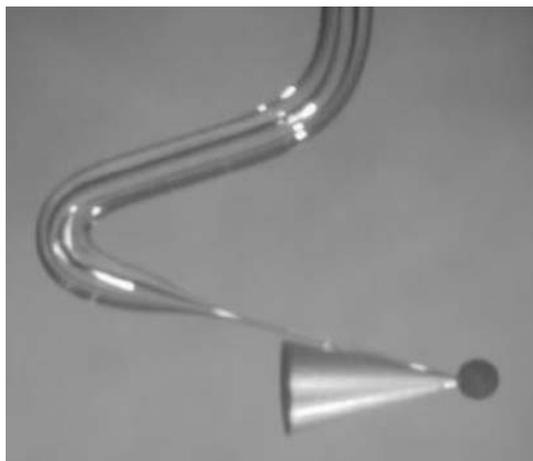


FIG. 8. A target consists of RF-PF shell for cryogenic DT experiment in FIREX-I. The capsule is covered with poly([2,2]paracyclophane) film.

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