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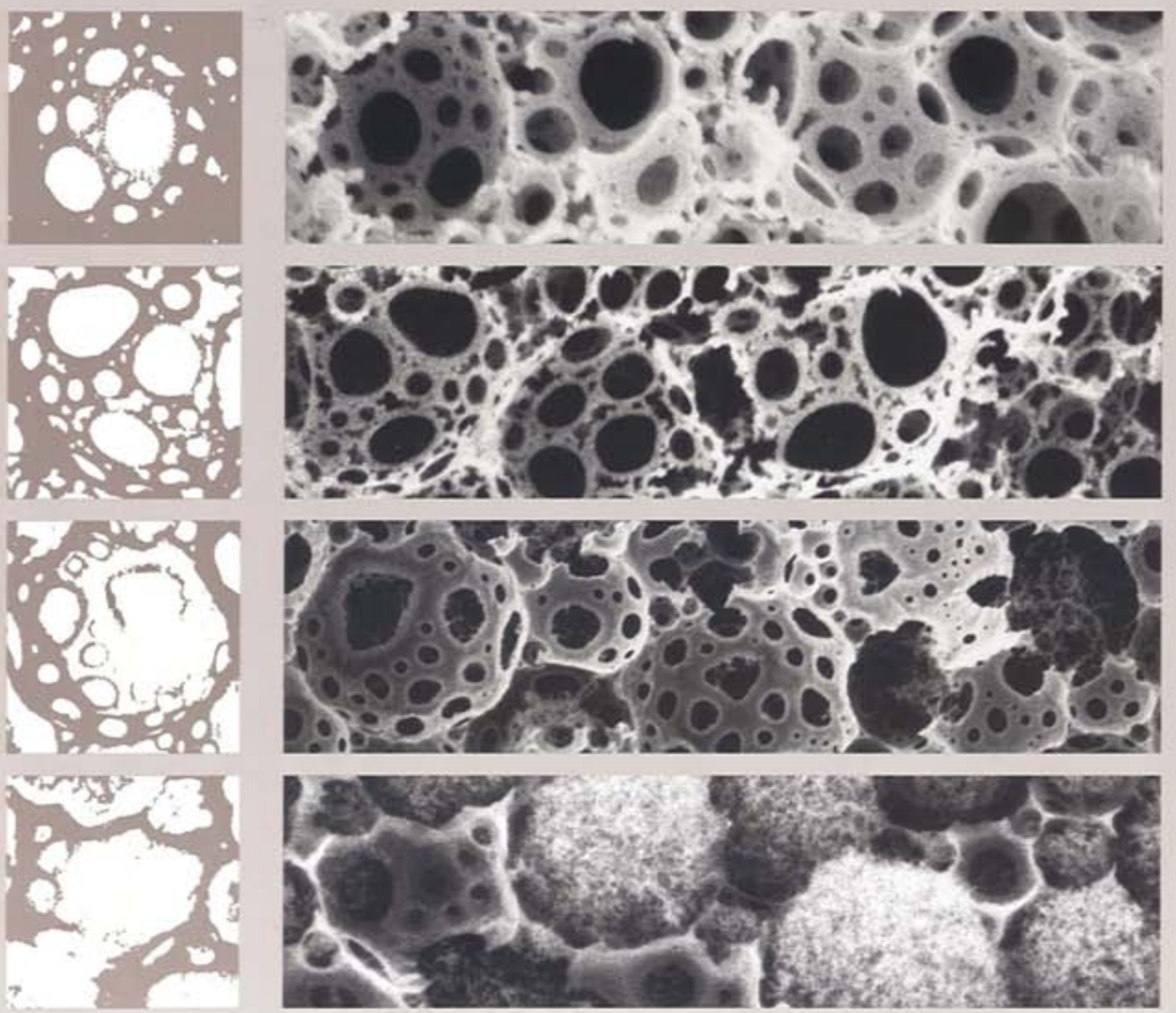

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Low-Density Polymer Foams for Fusion-Fuel Capsules

Laser inertial confinement fusion requires that the fuel in direct-drive targets retain certain characteristics before and during implosion. We have developed several low-density polymer foam candidate materials for confining the fuel in these targets.

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The process that generates the sun's energy is sustained nuclear fusion. Replicating this process on earth would yield a virtually inexhaustible supply of energy. A promising approach to this replication is direct-drive laser inertial confinement fusion (ICF): high-power laser beams directly and rapidly heat the surface of a target capsule, usually containing a deuterium-tritium (DT) fuel mixture, to form a plasma envelope. The rocket-like blowoff of plasma material from the surface (ablation) drives the capsule inward to compress and heat the fuel. The core of the capsule reaches a density about 10^3 times that of liquid DT and a temperature of nearly 10^8 K (8 keV). Under these conditions, a central hotspot ignites, and a thermonuclear burn spreads radially throughout the compressed and inertially confined main fuel layer.

The physics of the ICF burn imposes several requirements on the design and material characteristics of the fuel and capsule that constitute the direct-drive target. One requirement is the initial density of the DT fuel: its final imploded configuration is more easily achieved if the fuel starts in a condensed state, as a liquid or solid (depending on the density of the DT vapor required inside the capsule). Cryogenic temperatures (~20 K) maintain the DT in the liquid state. For the implosion to initiate fusion, the liquid fuel must be held in a shape with near-perfect spherical symmetry. Calculations have shown that the most favorable fuel configuration for direct-drive laser ICF is a shell. The vapor region at the core of the shell serves as a spark plug when compressed by the implosion. The target capsule must therefore hold the DT in this configuration. One approach to achieving this is shown in Figure 1, where the liquid fuel is held in a very-low-density foam sponge in the shape of a spherical shell.[1]

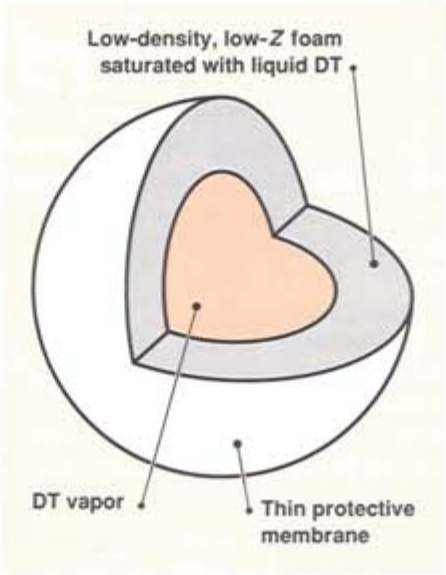

Figure 1. Use of a low-density, low-atomic-number foam to define and stabilize the configuration of the DT fuel capsule allows an attractive single-shell design for targets used in direct-drive inertial confinement fusion experiments. The liquid-DT-saturated foam provides both ablator and fuel. The DT vapor in the capsule interior provides an ignition hotspot. The capsule membrane provides a vapor barrier to prevent DT boiloff.

Requirements for an ICF Foam

The physics of direct-drive ICF require that the foam capsule have a certain combination of characteristics; it must be porous, low in density, and made of materials with low atomic number. Very-low-density foam material is mostly empty space and, if the foam cells are connected by pores (i.e., open-celled), will act as a wick. The DT will wet the foam and fill all the empty space, allowing the maximum possible amount of liquid fuel to fill the volume of the spherical shell.

For a wetted foam capsule, the internal structure must be sufficiently strong and small enough that capillary forces will support a liquid column about the height of the capsule diameter under the maximum acceleration that the capsule may undergo (~1000 *g*) during injection into a reactor at 1000 m/s. Each foam cell should be no more than 1 μm in diameter—more than 10 times smaller than can be seen with the naked eye. For maximum filling of the capsule and for virtually uniform

distribution of the liquid DT throughout, no cells can be closed or self-contained; all cells must be linked to all others by passageways.

The capsule foam must be as low in density as the need for structural integrity and machinability allows. We have been trying to achieve a density of 50 mg/cm^3. At this density, only 5% of the spherical volume is foam, leaving 95% of the volume available for filling with DT. Likewise at this density, only 5% of the material being burned is a contaminant rather than fuel. A final impetus for minimal density is that the foam structural members may introduce density inhomogeneities, which can grow catastrophically during implosion.

A variety of physical effects that can raise the necessary ignition temperature and reduce energy gain increase with foam density and atomic number; the foam must therefore be made of elements of low atomic number. Less than 1 at.% of the material can be composed of elements of atomic number higher than that of silicon, and less than 10 at.% can be composed of elements of intermediate atomic number between nitrogen and silicon. The most suitable range, because of the physics involved, is hydrocarbon (CH) foam—a material consisting only of carbon and hydrogen.

The foam must tolerate exposure to radiation from tritium without changing dimensions during the time needed for the target to fill and stabilize before implosion is initiated. Finally, the foam must be overcoated with a thin protective membrane of hydrocarbon material to prevent DT boiloff.

A variety of production techniques—such as droplet generator or molding techniques—seem to be adaptable to high-volume production of high-quality shells. There must be compatibility between the capsule material chosen and the high-yield fabrication process, and any subsequent characterization process must be automated.

Initial Research

To meet the criteria described, we looked for an organic polymer foam material, one with as few elements other than carbon and hydrogen as possible. We began our research by surveying the many foams commercially available at the time (1984). Most commercial foams have cell diameters that are hundreds of micrometers or larger (see Figure 2), as do natural low-density materials such as pith. The cell size in common foam cups, for example, is ~50 μm, and the cells are closed so that liquid cannot infiltrate. Filter membrane material commonly has a cell size in the appropriate range, but it is normally too dense, contains too high a percentage of atoms with an atomic number larger than carbon, and can be made only in thin sheets.

One promising candidate was a material used by the Porelon Corporation to make rubber-stamp ink pads; a mixture of polymer and salt dust is compressed and the salt is then extracted with water. Although we reached a cell size of a few micrometers by this process, we could not achieve adequate strength at densities lower than 100 mg/cm^3. And although silica aerogel is an inorganic polymer foam that meets our physical requirements, its atomic number is significantly higher than those of CH materials. Thus, we embarked on a materials development project to produce new organic foams.

When we began our foam development in the ICF Program in 1984, we focused on material made from ultrahigh-molecular-weight polyethylene (UHMW PE). We first had to learn to handle UHMW PE gels and to characterize them for structure. We soon were able to simplify our methods to the point

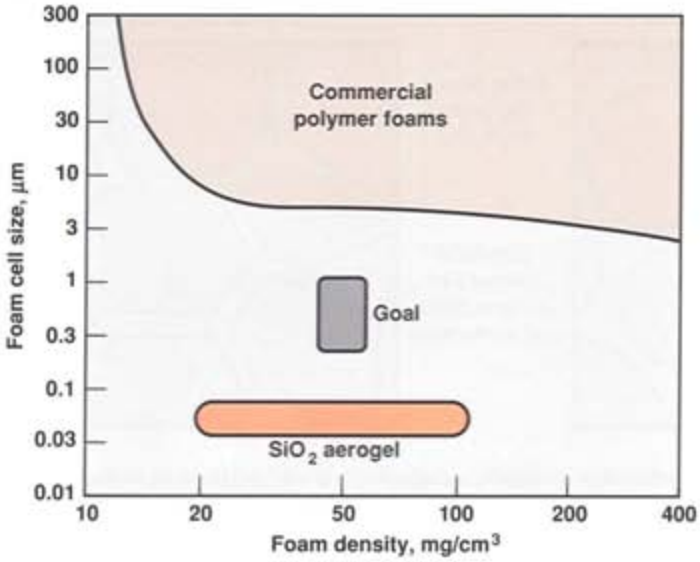

Figure 2. No commercially available hydrocarbon foams have the desired cell size and density. The SiO_2 aerogel meets these requirements but has too high an atomic number.

where we could make gels in a few hours without oxidative degradation. To make the foams, we first formed an entangled solution, generally in tetralin, of UHMW PE, with a molecular weight of $2–6 \times 10^6$ g/mol. We cooled the solution to gel it, crystallizing the polymer. Isopropyl alcohol replaced tetralin in the first solvent exchange, after which the gel was flushed with liquid CO_2 and then supercritically dried.

The ultrahigh-molecular-weight polyethylene met our density specification but presented problems of uniformity of density and seemed to harbor areas of closed cells that would not wick properly with liquid hydrogen. UHMW PE also was difficult to form without distortion and did not show high radiation stability.

We then performed a series of studies on carbon-fiber mats and rigid-rod polymers. Neither group of materials met all requirements.

Following these initial attempts, research in low-density polymer foams during the past few years has yielded much progress—and not only at the Laboratory.[2] In the process of developing several low-density materials, we have devised or improved methods of gelation and crystallization. We have used polymerization of an inverse emulsion system to make polystyrene (PS) foams; we have used gels formed by a condensation polymerization reaction to make resorcinol-formaldehyde (RF) and carbonized resorcinol-formaldehyde (CRF) foams; we have used phase separation to make cellulose acetate (CA) foams; and our newest foams are composites of PS and RF and a carbonized composite (CPR). Each of the materials studied has unique properties that give it its own set of advantages and disadvantages.

Polystyrene Foams

Polystyrene (PS) is an ideal low-density foam material for direct-drive laser ICF because its empirical formula is in fact CH. (The foam cups mentioned earlier are made of PS foams, but their properties are not suitable for our purposes.) Our investigation began when we received a response to an advertisement we placed in a technical magazine soliciting suitable candidate materials. Unilever Research Laboratory offered us the use of a system for making PS foams by polymerizing an inverse emulsion.[3]

Emulsions are familiar items, such as margarine, mayonnaise, and hand lotion. Emulsions are immiscible two-phase mixtures in which one phase is dispersed as small droplets in the other phase. Surfactants (surface-active agents) reduce the interfacial tension between the two phases and are used to stabilize the dispersed droplets in an emulsion. The magnitude and direction of the interfacial curvature characterize an emulsion: the curvature of the interface determines droplet size, and the direction of curvature determines whether an emulsion is regular or inverse. In a regular emulsion, the phase with the smallest volume is the dispersed phase, whereas in an inverse emulsion, the major phase is encapsulated within the minor phase.

The novelty of our investigative work with inverse emulsions is that we are polymerizing the emulsion and then removing the aqueous phase to produce a foam. Figure 3 shows two possible structures of inverse-emulsion systems; we use an inverse-emulsion structure to make PS foams that are intermediate between these two cases, with some droplets spherical and some polyhedral. As the figure shows, the internal phase is water that contains sodium persulfate ($Na_2S_2O_8$), and the external phase is an oil phase that is a mixture of two monomers, styrene and divinylbenzene (DVB), and an oil-

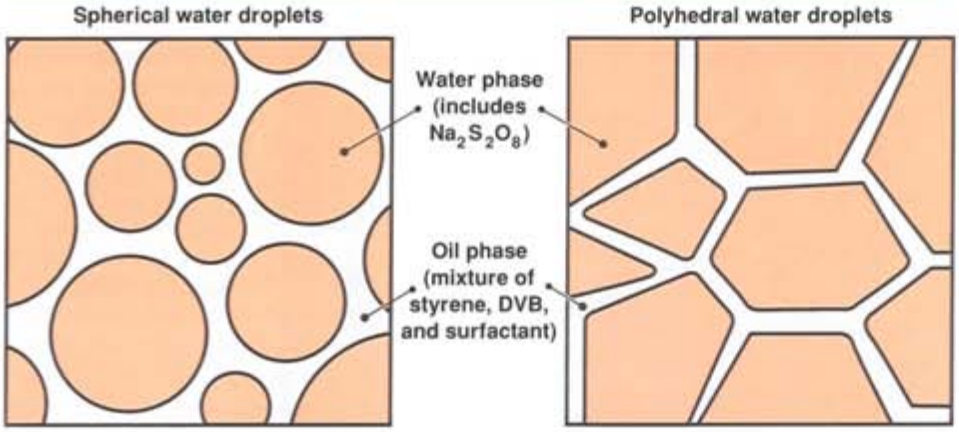

Figure 3. Two extremes of emulsion structure, using spherical and polyhedral water droplets. Geometrical calculations indicate that spherical droplets must show a distribution of droplet sizes; polyhedral droplets can be uniform in size.

soluble surfactant. The surfactant is sorbitan monooleate, manufactured by ICI Americas, Inc., under the tradename Span 80. The water phase constitutes from 92 to 95% of the total material. The two phases are mixed to form the emulsion, and the system is heated to 50°C for 24 h, causing the sodium persulfate to initiate a polymerization reaction of the styrene and DVB as shown in Figure 4. When this polymerization is complete, all the thin interfacial regions have formed a solid PS material that surrounds the water droplets. Oven drying these foams produces spaces where the water droplets had been, yielding a low-density material ranging between 50 and 80 mg/cm^3.

Much of our early work with this system centered on finding the optimum formulation with respect to minimizing cell size while maintaining uniformity of structure. As with most emulsion systems, the key to this process is the surfactant. The surfactant stabilizes the thin interfaces of the oil phase and keeps the system from coalescing into larger droplets or from breaking into two separate phases. We have found that only sorbitan monooleate can accomplish this successfully, and the reasons for its uniqueness are not completely understood. The amount of surfactant is also critical, and cell size, density, and surfactant concentration are related. The smaller the desired cell size or the lower the density, the more surfactant must be used to stabilize the oil phase, which must spread itself more and more thinly as the cell size or density decreases. Theoretical studies have shown that, at the density we require, there is a lower limit of approximately 2–3 μm cell size, since the interfaces would have to be impossibly thin if the cells were any smaller. As we have seen, however, the desired maximum cell size is 1 μm.

We have also investigated how different mixing devices affect the cell size of the emulsion. The most effective device is one that we developed from a concept first advanced by Los Alamos researchers.[2] Called a syringe pump, it mixes by forcing the emulsion back and forth through a small orifice between two syringes. We believe that passing the droplets through the orifice elongates them and causes them to break up into smaller droplets, and the lack of high shear keeps the emulsion from breaking. This pump achieves the lower limit of 2–3-μm cell size.

One key success in our research with PS foams has been the development of a process for extracting impurities from the foam without damaging its structure. Both the initiator and the surfactant leave decomposition products in the foam that are impurities because they contribute extra mass and are of too high an atomic number. Through x-ray diffraction studies of small crystallites that scanning electron microscopy reveals in the foams, we

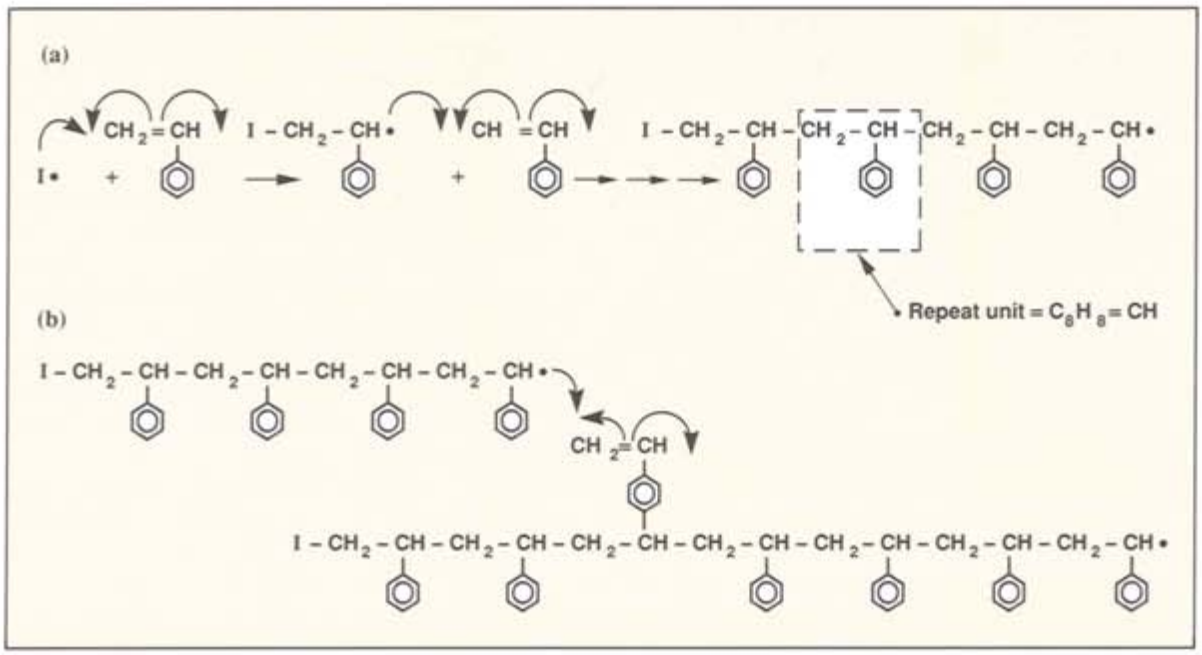

Figure 4. (a) Initiated by free radicals (I•), chain polymerization of styrene and divinylbenzene (DVB) monomers forms polystyrene (PS) foams. (b) DVB allows crosslinking between different growing chains.

have established that the initiator, sodium persulfate, decomposes to a mixture of sodium sulfate, Na_2SO_4, and sodium bisulfate, $NaHSO_4^-$. These are impurities of very high atomic number that would substantially interfere with the required density uniformity. We studied surfactant decomposition by Fourier transform infrared spectroscopy (FTIR) of thin slices of foam. We established that some of the surfactant remains as sorbitan monooleate and some hydrolyzes to form oleic acid and sorbitol.

We developed an extraction apparatus that forces a mixture of isopropanol and water through the foams to remove virtually all of these impurities. The effects of this process are graphically illustrated in Figure 5, which compares x-radiographs of unextracted and extracted foams. The dark rings are caused by the initiator decomposition products, which are significantly more opaque to x rays than is CH. Since the surfactant contains only carbon, hydrogen, and oxygen, its removal does not show up significantly in radiography, but it has been confirmed by FTIR and by weight-loss calculations.

Building on our ability to remove the surfactant from PS foams, we lowered foam density further while maintaining the desired cell size. We increased the amount of surfactant in the oil phase to create more stable emulsions, with less tendency to coalesce and form larger cells or voids; then by removing this surfactant and its decomposition products after polymerization, we lowered the density even further. This approach eventually allowed us to achieve our goal of 50 mg/cm^3. We could not lower the density past this point by this method because there is an upper limit to how much surfactant can be incorporated into the oil phase without undesirable changes in foam structure.

(a) Original foam sample (b) After extraction

Figure 5. X-radiographs of extracted and unextracted polystyrene foams. (a) The original, unextracted foam sample (1 cm thick by 2.3 cm in diameter) has a density of 94 mg/cm^3. (b) After extraction, density is 71 mg/cm^3. The extraction process removes high-Z impurities that cause the rings seen in (a).

We tried extending this idea even further by incorporating ethylbenzene, the nonpolymerizable compound closest in structure to styrene, into the oil phase as a diluent. After polymerization, the same extraction procedure was found to remove the ethylbenzene, thus lowering the density still further. With this approach, we achieved a density of 30 mg/cm^3. This marked the limit of this procedure, as this foam barely had enough mechanical strength to undergo the extraction process. Thus, our development of this system has fully investigated and explored the limits of what can be achieved with this chemistry.

In Figure 6, we show scanning electron micrographs of foams made by the standard process, achieving a density of 50 mg/cm^3, and a foam made with the incorporation of ethylbenzene, achieving a density of 30 mg/cm^3. The key feature of PS foams from the standpoint of direct-drive laser ICF is that they are open celled, with pores connecting the cells that are approximately 1 μm in diameter. This open-celled structure gives these foams good wetting properties with liquid DT. The studies that we have done indicate that it is the size of the pores that determines the wetting behavior, so the fact that the cells are 2–3 μm in diameter is not a problem for wetting.

PS foams are good candidates for direct-drive laser ICF. They have excellent machinability and are extremely easy to work with, and PS is known to have good radiative stability. As mentioned above, the DT wetting behavior is quite satisfactory. The major disadvantage lies in the 2–3-μm cell size, which, although it does not appear to cause

problems with the wetting properties, does make it virtually impossible to achieve the very fine surface finishes (1 μm) that may be required. Also, the scalelength for material discontinuity may be too large, which might adversely affect the implosion dynamics.

Resorcinol-Formaldehyde (RF) and Carbonized RF Foams

Primarily because of the large cell size of the PS foams, we have sought other low-density foam materials. Our most promising development so far has been foams based on the condensation polymerization reaction between resorcinol and formaldehyde. Although this chemistry has been known for some time, the idea of adapting it to make low-density materials is relatively new.[4]

Resorcinol and formaldehyde are mixed in aqueous solution in an approximately 1:2 molar ratio in the presence of sodium carbonate, which controls the pH of the reaction and hence the rate of polymerization. After stirring, the solution is sealed in glass containers and heated at 90°C for seven to nine days. During this time, a gel forms and a substantial amount of crosslinking occurs. After the curing process is complete, a series of solvent treatments and exchanges leading to supercritical drying from liquid CO_2 is performed. The dry RF foams are red in color and are transparent to high-intensity light. Foams with densities of 20–200 mg/cm^3 have been synthesized.

As with the PS foams, considerable experimentation was directed toward determining optimum formula and procedure. Statistically designed experiments played a key role in determining the critical function of sodium carbonate concentration in minimizing RF foam shrinkage, thus leading to the required low densities.

Much of our investigation has focused on how the process of gelation occurs. Although this is not yet firmly established, we do know from scanning electron microscopy

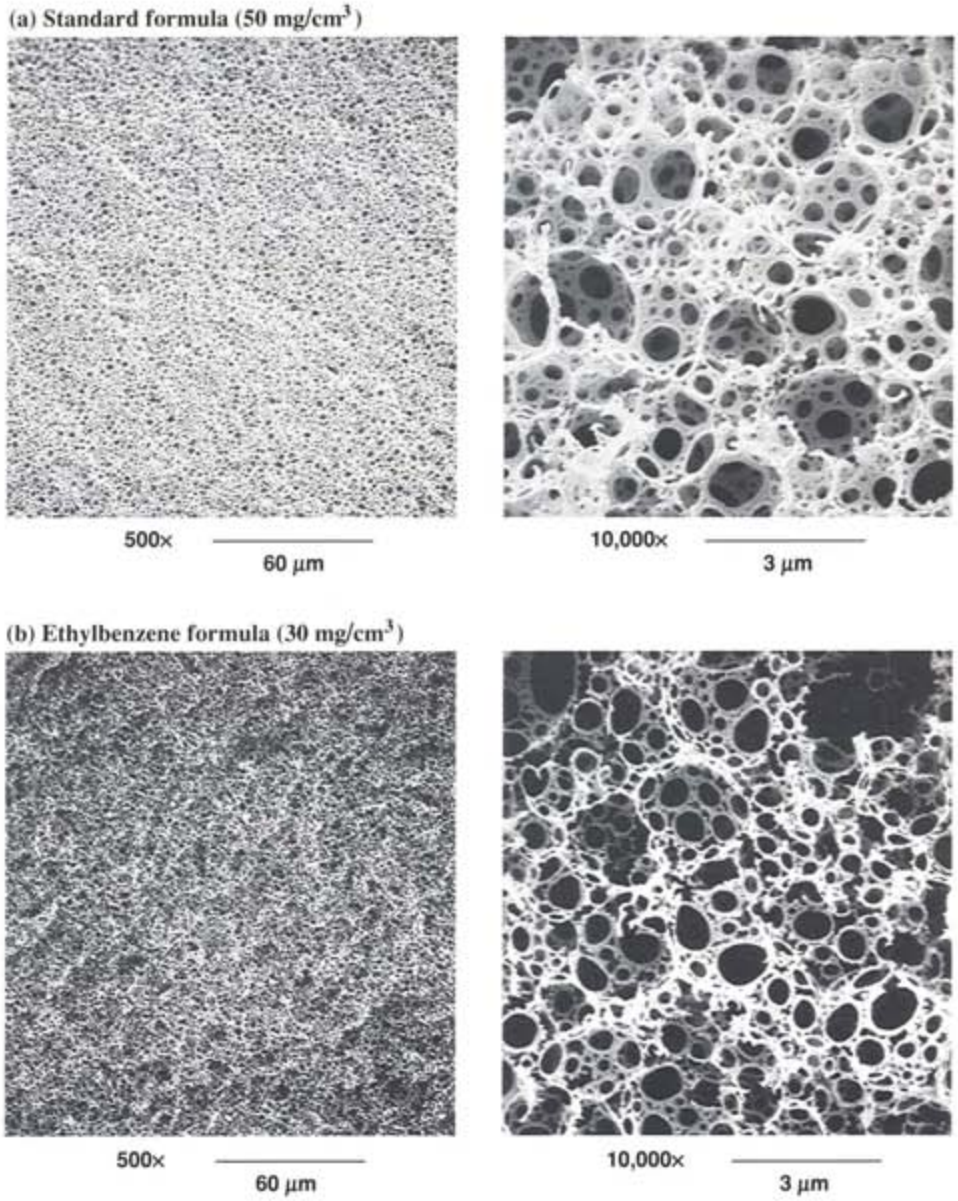

Figure 6. Scanning electron micrographs of polystyrene foams. The left image of each pair shows 500× magnification, the right shows 10,000× (a) Standard formula, 50 mg/cm^3. (b) Ethylbenzene formula, 30 mg/cm^3.

and transmission electron microscopy that the final structure is that of beads on a string, with each bead approximately 3–13 nm in diameter, depending on the concentration of the catalyst. A schematic diagram of a possible pathway for the gelation process is presented in Figure 7. Light and neutron scattering experiments currently under way should shed additional light on the mechanism.

RF foams are extremely difficult to handle, being very fragile and tacky. We eventually determined that they also lack the required machinability. Fortunately, RF foams respond well to carbonization—the process of heating a material to elevated temperatures in the absence of oxygen to remove nearly all elemental components except carbon without significantly impairing macroscopic structural integrity. Not all polymers can be successfully carbonized, but RF foams can be; this process dramatically increases their mechanical strength, probably by converting the remaining carbon to a graphite-like structure.[5] This carbonized resorcinol-formaldehyde (CRF) foam is currently our best prospective material.

Although the process of carbonization does increase mechanical strength, it also causes some shrinkage. However, the RF foams can be made with a low enough density so that the objective of ~50 mg/cm^3 can still be achieved after carbonization. There are also problems with cracks forming in the foams during carbonization, and much of our current work is focused on optimizing this process to minimize shrinkage and cracking.

The scanning electron micrograph of CRF foam shown in Figure 8 reveals the structure described earlier. The cell size, although not as well defined as in the PS case, is clearly less than 0.1 μm. This leads to excellent wetting properties for CRF foams and should also make it possible to achieve the required surface finishes. There is insufficient information in the literature about the radiative stability of this material, so we will have to test that ourselves.

Cellulose Acetate Foams

While we investigated RF and CRF foams, we were also investigating cellulose acetate (CA) foams, which have some attractive properties. We developed a process for making low-density CA foams by a phase-separation method. We prepare a very-low-weight-percent solution in benzyl alcohol and cool it below the phase-separation temperature. By this method, we have obtained foams with densities of ~30 mg/cm^3.

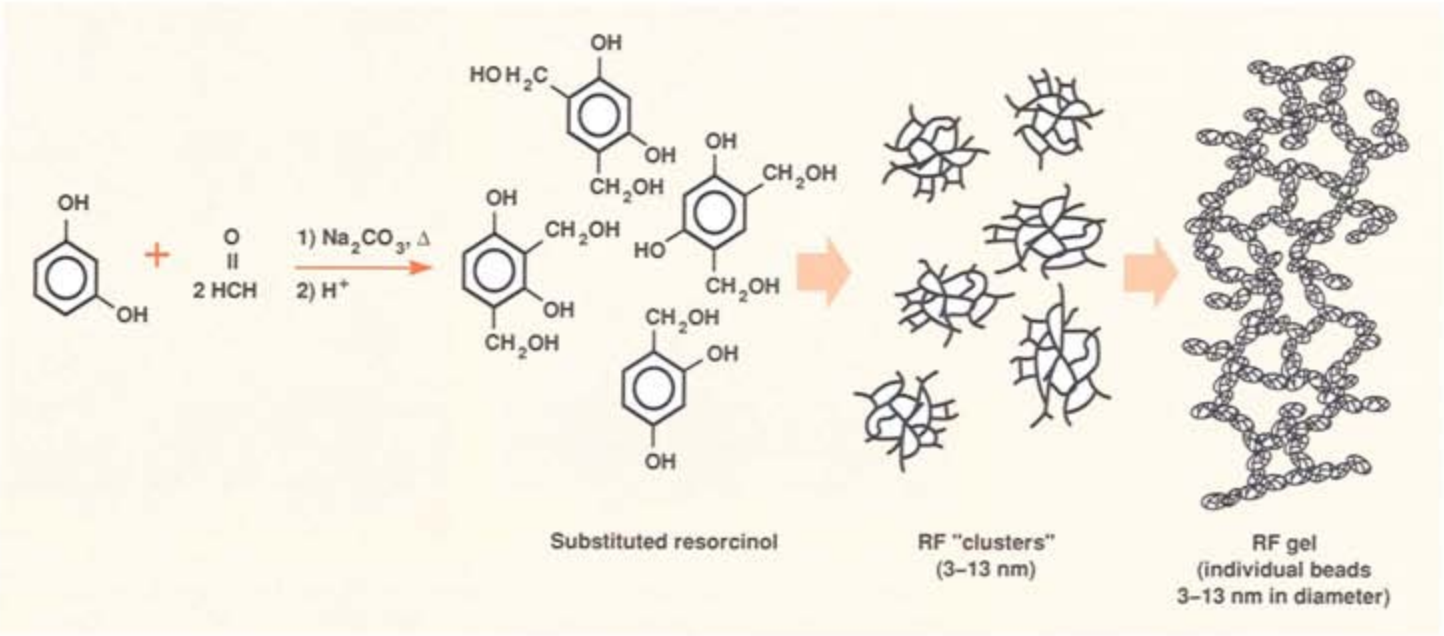

Figure 7. Schematic diagram of a possible resorcinol-formaldehyde (RF) gelation mechanism, showing formation of clusters that eventuate in a "beads-on-a-string" gel structure.

One attractive feature of the CA foams is their outstanding moldability, which could be important in processes in which machining is impractical because very large numbers of parts have to be prepared. However, calculations and preliminary experiments have shown that the radiative stability of this material is not sufficient for the ICF application, so we have discontinued research on these foams.

Composite Foams

Taken separately, PS foams and RF foams have roughly complementary sets of advantages and disadvantages. To see whether we could combine the advantages of the two foams, we recently produced composites of the two materials.[6] We prepare a PS foam and impregnate it with an RF solution. Processing yields a composite PS/RF foam. As shown in Figure 9, the composite foam retains the cell structure of the PS foam, and the RF beads on a string fill the cells. As expected, the presence of the PS matrix makes this material much stronger than RF alone. Because the RF foam does not uniformly fill the PS structure, the PS matrix still determines the cell size of these foams (i.e., 2–3 μm).

Research with these PS/RF composite foams has yielded one surprising discovery. It has long been known that PS foams cannot be carbonized; attempts at carbonization simply yield a very small residue of decomposition products. By contrast, these PS/RF composite foams can be carbonized. The weight remaining after carbonization corresponds to the amount of RF, indicating that the PS decomposes as expected, but its structure remains, as shown in Figure 10. The likely explanation

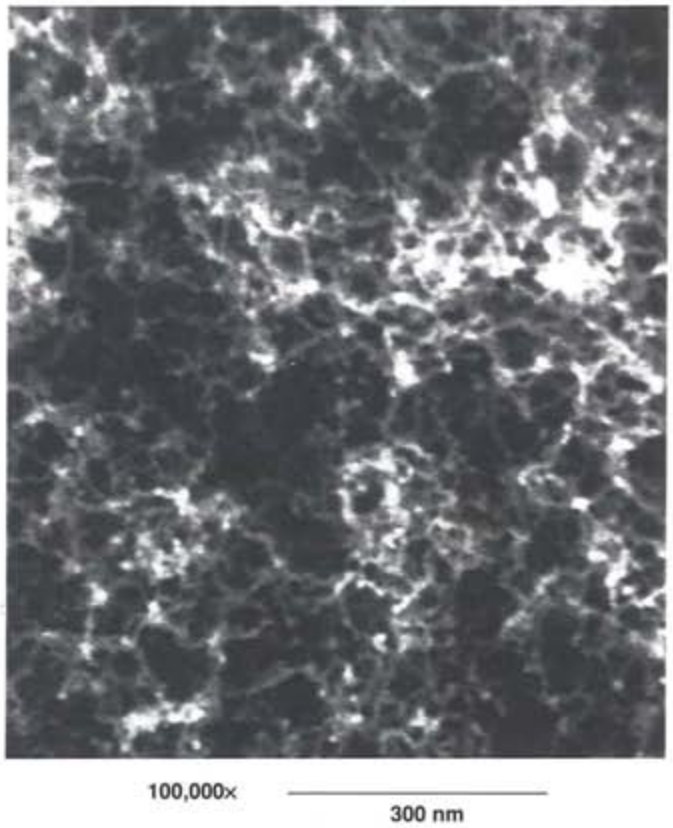

Figure 8. Scanning electron micrograph of carbonized resorcinol-formaldehyde (CRF) foam, 35 mg/cm^3.

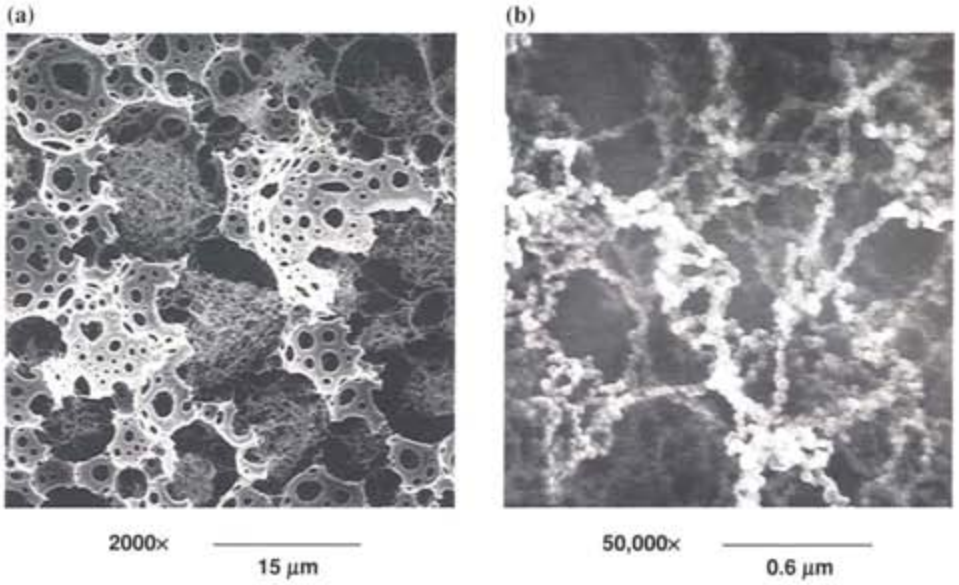

Figure 9. Scanning electron micrographs of PS/RF showing the cellular structure of PS and the interconnected bead structure of RF. (a) PS/RF foam, 66 mg/cm^3. (b) Closeup of RF beads.

is that there is a stage during carbonization when the RF behaves in a plastic manner and the PS acts as a template for the RF. The RF maintains its beads-on-a-string structure in the areas between the PS cell walls, but also assumes the morphology of these cells. This templating process could be of considerable interest in polymer chemistry.

Summary

In our pursuit of low-density materials for direct-drive laser ICF, we have been quite successful in producing several promising candidates. We have also developed several new materials that, although not suitable for this application, may find important uses wherever extremely low-density materials with good mechanical properties may be required. In the process of this work, we have discovered several unexpected foam characteristics that may have important implications in the larger fields of polymer and colloid chemistry.

We are focusing current efforts on improving the quality of our CRF foams by developing more reliable production procedures and methods of measuring density uniformity.

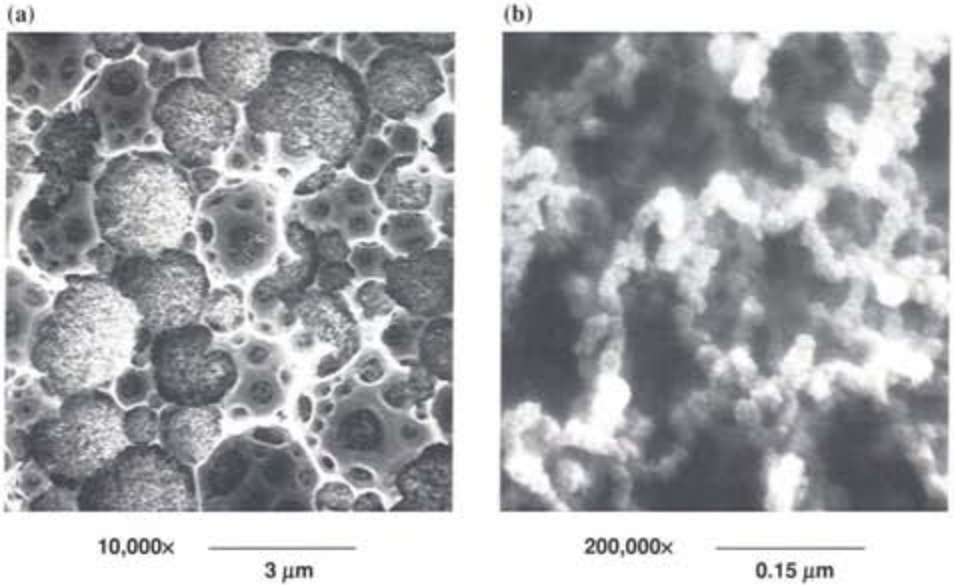

Figure 10. Scanning electron micrographs of carbonized composite foam (CPR) with a density of 67 mg/cm³. (a) Low magnification shows PS-type cell structure filled with RF-type structure. (b) Closeup of CRF structure inside PS-type cells.

Key Words: fusion—direct-drive laser inertial confinement; polymer foams—carbonized resorcinol-formaldehyde, cellulose acetate, polystyrene, resorcinol-formaldehyde.

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