Low-Density Hydrocarbon Foams for Laser Fusion Targets

Progress Report—1986

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Abstract

We describe progress made during 1986 in the development of direct-drive hydrocarbon foam targets for laser fusion. The foam materials are polystyrene and resorcinol-formaldehyde. The processes for making the foams, their properties, characterization techniques, and the relationships of their properties to target specifications are presented. In the final section, we discuss statistical experimental design techniques that are being used to optimize the foams.

Introduction

We are developing foams for the direct-drive, high-gain ICF target that is described in the 1985 *Laser Program Annual Report*¹ and in a paper by R. A. Sacks and D. H. Darling.² This target design calls for a spherical shell of foam that can be wetted with liquid DT. The liquid DT is both fuel and ablator: the foam holds the DT in a spherical-shell configuration that is compressed to high density and ignited by the laser energy. The foam must have a density of 0.05 g/cm³ and be composed mainly of carbon, hydrogen, and oxygen; less than 1% of the material can be elements of higher Z than silicon. In addition, the foam should have a cell size of less than 5 μ m to meet uniformity requirements and a pore size of less than 1 μ m to stably hold the liquid DT. The foam must tolerate exposure to the radiation environment of tritium without changing dimensions during the time needed for the target to fill and stabilize before a shot. The foam must be machinable or moldable to the required spherical-shell configuration and tolerances. Also, some target designs will require a foam with an overcoat of approximately 5 μ m of a hydrocarbon (CH) or other low-Z material.

In 1985, we began measuring and comparing the properties of polyethylene (PE) and polystyrene (PS) foams. Early in 1986, we found three problems with the PE foams: uniformity did not meet our specifications, machinability was poor, and the rate of liquid wetting was very low. We tried to resolve these problems while simultaneously researching our PS foam material. We discovered that the PS foams were superior in machinability and liquid-wetting characteristics. Voids within the material presented a uniformity problem, but we felt this could be solved with proper processing. We therefore dropped PE foam research and concentrated all our efforts on the PS foam.

Several properties of the PS foam, including its cell size, pore size, air bubble content, density uniformity, and emulsion stability presented diffi-

cult materials-development problems. In the first section of this report, "Polystyrene Foams," we discuss the emulsion preparation, including its formulation, processing, and properties. The characteristics of the foams are then discussed in relation to target specifications.

We have also started research on resorcinol-formaldehyde (RF) gels from which foams can be prepared. These materials have much finer cell size than PS foams do. The formulation, processing, and properties of the RF foams are discussed in the section "Resorcinol-Formaldehyde Foams." These foams, because of their small cell size, offer potentially greater DT-fill stability than the PS foams.

In the final section, "Experimental Design for Foam Optimization," we discuss procedures to optimize the formulation of the foam materials. The preparative methods have many formulation and processing variables. To efficiently determine optimum conditions, we are using statistically designed experiments in our investigations.

Foam development progressed rapidly in 1986. We are now able to make uniform 2- to 3- μ m cell size, 1- μ m pore size PS-foam material with a density of 0.05 g/cm³. With the new RF foam material, we propose to reduce the cell size to 0.1 μ m. We developed techniques to measure foam uniformity, mechanical properties, and the rate of liquid flow into foams. Problems with density variations and voids within the foam were solved. The foams were tested for liquid hydrogen wetting and performed well.

We will continue the PS foam production and determine the potential for developing the new RF foam. Molding and machining techniques will be developed to make the final shell configuration for the foams, and we will establish bonding techniques to hold foam hemispheres together. We will also pursue any promising leads to new foam materials.

Polystyrene Foams

Introduction

Our process for making PS foams is based on an inverse-emulsion system originally developed by Unilever Research Laboratory.³ A water-in-styrene

(w/s) high-internal-phase emulsion (HIPE) is made by using a surfactant such as sorbitan monooleate (Span 80) and a w/s ratio of 90/10 or 95/5. The emulsion is then thermally polymerized and the resulting foam is dried in a vacuum oven. The

structure of the foams and the details of the process for making them are described in Ref. 4.

Our development of the chemistry of this system included investigating alternative surfactant systems and looking at the effect of salts on emulsion stability. We used different polymerization initiators and varied the initiator concentration, the temperature of polymerization, and the amount of divinylbenzene (DVB), which is used as a cross-linking agent. Because the properties of the emulsion are directly related to those of the resulting foam, we have used optical micrographs of the emulsions as well as scanning electron micrographs of the foams to investigate these changes.

We experimented with a variety of mixing techniques for the emulsion system, to improve uniformity and decrease cell size in the foam. We also tried to induce the polymerization with radiation rather than thermally.

To increase our understanding of the emulsion system, we investigated two areas of fundamental significance for emulsion stability: the interfacial tension of the styrene/water/surfactant system; and the relationships between the geometric constraints of the emulsion and its cell size, interfacial thickness, and density of the resultant foam.

A major focus of our foam development work was determining the performance of the foams with respect to the structure and uniformity specifications for laser targets. We also looked at the machining and wetting characteristics of the foams and at those mechanical properties related to their end use.

Foam Preparation

Emulsion Chemistry

Because the foam structure is essentially a polymerized replicate of the emulsion structure, it is very important to minimize coalescence by producing the most stable emulsion possible, and to process the emulsion under conditions that maintain this stability. This will allow us to produce a foam with the minimum cell size.

Surfactants help stabilize emulsions by lowering the interfacial tension in a manner that produces the correct interfacial curvature, that is, the curvature that results in the desired phase becoming the internal phase. To get a stable emulsion, we must have the right hydrophilic/lipophilic balance (HLB), the right chemical type, and the right concentration of surfactant. For our high-internal-

phase inverse emulsions, the HLB value should range from 3 to 6. We are investigating chemical types and concentrations. We studied individual surfactants such as Span 80 and divalent metal soaps, as well as blended surfactants such as dodecyl alcohol/Span 80 and mixtures of Spans and Tweens (polyoxyethylene sorbitan esters).

Unilever Research Laboratory uses Span 80 in its process. For our emulsions, Span 80 can stabilize them as long as its concentration is higher than 10 wt% and lower than 50 wt% of the oil phase (which includes the monomer(s) and the surfactant). Most of the resultant foams have an open-pore cellular structure. However, a foam made with an amount of Span 80 equal to 50 wt% of the oil phase did not have a porous structure and crumbled easily. The best foam, with the smallest cell size, was made with 20 wt% Span 80, while one made with 10.5 wt% Span 80 had a substantially larger cell size, as shown in Fig. 1. The cells exhibit both spherical and polyhedral shapes.

Although their HLBs are not known, divalent metal soaps are said to give stable water-in-oil emulsions because the metals form bridging structures that give the right interfacial curvature. We attempted to make emulsions with barium stearate, calcium oleate, and magnesium stearate, but none of these stabilized an emulsion as well as Span 80.

Blends of surfactants are often much more effective than any individual surfactant. The preliminary findings of our investigation of surfactant mixtures are:

- A mixture of Span 80 with dodecyl alcohol as cosurfactant gave an emulsion that was not as stable as one made with Span 80 alone. Water droplet coalescence could be seen in the emulsion under the optical microscope. The resultant foam had a very large cell size (100 μ m).

- Combinations of Spans and Tweens with HLB values ranging from 3 to 6 were tried. We found that:

- No emulsions can be formed in the presence of Tween.

- The stearate family does not seem to be the right chemical type.

- A mixture of Span 80/Span 40 (sorbitan monooleate/sorbitan monopalmitate) with an HLB of 5.5 gave a satisfactory emulsion, but not substantially better than Span 80.

These results are consistent with those obtained by Unilever and with an examination of the chemical structures of the surfactants. The polyoxyethylene chains on the Tween surfactants are strongly hydrophilic, which probably gives

Figure 1. Scanning electron micrographs showing the effect of surfactant concentration on foam cell size: (a) 10.5 wt% Span 80, (b) 20 wt% Span 80.

the wrong interfacial curvature. The most effective individual surfactant should have a lipophilic structure similar to that of the monomer phase. Thus it would be expected that the unsaturated oleates would be more compatible with the unsaturated styrene than would the saturated stearates, and this is what we found.

A Lever Brothers patent⁵ indicates that addition of a trivalent salt, particularly AlCl_3 , at 2 to 4 wt% of the water phase will improve emulsion stability. We found that the addition of salt to the aqueous phase does enhance emulsion stability, as measured by the rate of coalescence. We compared the enhancing abilities of sodium chloride, calcium chloride, and aluminum chloride in emulsions made with an amount of Span 80 equal to 20 wt% of the oil phase. Our results show that 0.1 wt% of AlCl_3 gives the greatest stability. Figure 2 illustrates the effect of AlCl_3 addition on the rate of droplet coalescence. The micrographs show that the water droplets in the control sample coalesced much faster. The droplets were bigger, and their shape changed from spherical to polyhe-

dral after 20 min at 50°C. (Ethylbenzene, rather than styrene, was used in this experiment because no polymerization was planned.)

Time and temperature also affect the stability of emulsions. We found that given sufficient time, on the order of days, our emulsions coalesce and eventually break. This is caused by the emulsion's tendency to minimize surface energy. Coalescence accelerates with increasing temperature. The coalescence rate demonstrated by the micrographs in Fig. 2 is substantially higher than that observed at room temperature. At 70°C, the emulsions show large areas of coalescence within a few minutes.

Polymerization of the Emulsions

Polymerization is initiated by the thermally induced dissociation of an unstable molecule, the initiator, which generates a free radical. The free radical opens the π -bond of the monomer molecule and propagates the reactive center to the end of the monomer. This species then reacts with another monomer, and the reactive center moves to

Figure 2. Water droplet coalescence in emulsions of ethylbenzene, Span 80, and water is hindered by the addition of AlCl_3 . (a) Control; (b) with 3% AlCl_3 .

the end of this second monomer. This process is repeated many times in a chain manner to produce a polymer molecule.

Although the process normally uses sodium persulfate as the polymerization initiator, we also tried using benzoyl peroxide because the elimination of residual sulfur in the foams is desirable. Benzoyl peroxide was dissolved in the monomer

phase at three concentrations of 0.5, 1, and 2 wt% of the water phase. The foam made with 0.5 wt% benzoyl peroxide is the best of the three, but it is more rubbery and fragile than those made with sodium persulfate. We may be able to correct this problem by using lower concentrations and a higher polymerization temperature.

The ideal process of polymerization requires minimizing the polymerization time, so as to "lock in" the foam structure before any substantial coalescence occurs. However, both the coalescence rate and the polymerization rate depend on the temperature, so it is necessary to balance these two effects. The polymerization rate also depends on the initiator concentration and affects the molecular weight of the foam. The highest-molecular-weight polymer, which should also have the highest strength, is generated at the slowest polymerization rate. Accordingly, we designed an experiment to study the effect of temperature and initiator concentration on the structure, molecular weight, and mechanical properties of the foam. We investigated a series of four initiator concentrations (2.4, 4.8, 9.6, and 14.4 g/L) and three polymerization temperatures (40, 50, and 70°C) centered at our best present conditions. After polymerization, differences among the materials were immediately observable. Emulsions that were polymerized at high temperature tended to shrink as a result of coalescence. Emulsions that were polymerized rapidly at either high temperature or high initiator concentration were very brittle and crumbled when touched, because of the low molecular weight and the resulting low mechanical strength.

Each of the foams was examined on the scanning electron microscope (SEM) to determine the cell structure. We found that the cell size is independent of initiator concentration and polymerization temperature. However, there were differences in the cell and pore structure. At low polymerization rates, many of the pores in the foam remained closed by a thin membrane [Fig. 3(a)]. Higher rates led to enlarged pores [Fig. 3(b)]. At the highest rate, the structure became thin and weak [Fig. 3(c)]. The polymerization rate, therefore, offers a means of controlling the pore size of the foam.

In the foams made for this experiment, we did not add any cross-linking monomer; therefore, the molecular weight could be measured and used to analyze the reaction kinetics. The dried polymer foams were dissolved in tetrahydrofuran and the molecular weight was determined by gel permeation chromatography. The molecular weights ranged from 30,000 to 300,000. The highest molecular weight was produced at the lowest temperature and initiator concentration, as expected. The lowest molecular weight foams were brittle, while the highest molecular weight foams were very hard to cut. After analysis, the results will allow us to predict and control the foam mechanical properties through the conditions of the polymerization.

We also studied the effect of the cross-linking agent DVB on cell structure and foam properties. The concentration of DVB was varied from 0 to 100 wt% of the monomer used. The amount of Span 80 was 20 wt% of the oil phase. Scanning electron micrographs of all the foams indicate that they have an open-pore cellular structure. The pore size decreases with increasing DVB concentration (from 1.4 to 0.9 μm), but the cell size remains at 5 μm .

At this point, the combination of factors that produces the best foam appears to be a 50:50 ratio of styrene to DVB, an amount of Span 80 equal to 20 wt% of the oil phase, an initiator concentration of 1.0 wt% of the water phase, and a polymerization temperature of 50°C. This foam is shown in Fig. 1(b).

Another way to shorten the polymerization time was to replace thermal treatment with gamma radiation. Thermal polymerization takes about 24 h at 50°C, while gamma radiation, if successful, may take just a few minutes. The ^{60}Co radiation source used provides two dose rates: 12 and 74 krad/min. After a number of experiments, we found that the dose rates were not appropriate for our application. No change occurred at the low dose rate, and a stable emulsion would undergo phase inversion after 2 h of exposure at the high dose rate. Although radiation-induced polymerization of pure styrene is a common technology, our system is different in that we have so much water (90 to 95% by weight) in the mixture. While the polymerization rate could be much lower because of the presence of the water, the gamma rays could also attack the water molecules and form hydroxyl radicals. These radicals could then attack the surfactant and break the emulsion. We are still trying to discover the actual mechanism for breaking the emulsion before we proceed further.

Mixing Techniques

Another area of substantial investigation was the identification of mixing techniques for the emulsion. The parameters associated with mixing can have a direct effect on the cell size and uniformity of the resultant foams.

To produce most emulsions, it is necessary to expend mechanical energy. The mechanical energy counteracts the minimization of surface energy, which the system tries to accomplish through coalescence. Mechanical energy in the form of shear elongates the droplets and breaks them up into smaller droplets. For several reasons, our emulsions present special mixing problems. First,

(a)

(b)

(c)

15 μm

Figure 3. Scanning electron micrographs showing effects of polymerization rate on foam cell and pore structure: (a) 4.8 g/L initiator, 50°C; (b) 9.6 g/L initiator, 50°C; (c) 4.8 g/L initiator, 70°C.

these high-internal-phase emulsions contain only 5% of the material as the continuous phase and 95% as the dispersed phase. Hence, they are very sensitive and coalesce easily. High shear is needed

to achieve the desired 2- to 5- μm cell size. However, turbulence must be avoided to prevent coalescence. Second, as the cell size becomes finer the viscosity of the emulsion increases and the

emulsions eventually have a paste-like consistency. Producing uniform, high shear in such viscous fluids is difficult. Third, mixing must be accomplished without entraining air bubbles. To accomplish emulsion mixing, we tried stirring and pumping techniques.

We used three stirring techniques: a paddle, a blender, and a counter-rotating mixer. The first and simplest technique was a paddle stirrer. The problem with the paddle is that it produces a vortex around the stirrer shaft, which can cause air to be mixed into the emulsion. In a low viscosity medium, air bubbles rise to the top, but our emulsions have high viscosity so this did not occur. A tight-fitting top can be used to eliminate the air-emulsion interface, but preparation of these emulsions requires slow addition of the internal water phase. Thus, the volume of the emulsion grows by a factor of 20 during the addition of water. We used a blender, which is a closed-volume mixer; however, we abandoned this technique because of poor uniformity and leakage at the stirrer shaft, which introduced air. The counter-rotating mixer is a stirring technique we found useful in preparing and evaluating emulsion formulations. Here, two paddles mounted on coaxial shafts rotate in opposite directions to avoid producing a vortex. It is possible to prepare a well-mixed emulsion, but the intensity of shear is limited by turbulence at high stirring speeds, which causes the emulsion to invert to an oil-in-water emulsion. Hence, a uniform but not refined (in the sense of not having a small cell-size) emulsion can be prepared by this technique.

Pumping produces high shear by flow through fine orifices. It is closed-volume to avoid air introduction and adaptable to molding techniques in which the emulsion is pumped into the mold. We tried three pumping techniques: gear, piston, and peristaltic. In the gear pump system, a closed but expandable piston volume recirculated through the pump. This positive-displacement pump is capable of producing pressures high enough to force the viscous emulsion through the tubing. Two forms of piston pumps were used: a pair of joined syringes and a commercial, high-pressure, piston-pump homogenizer. The syringe technique provided our best material. Because it is a totally closed system, there are no sources of air to produce bubbles. The chief disadvantages are that it is difficult to maintain a good seal on the plunger and that only a small amount of foam is produced. The commercial, high-pressure homogenizer forces the emulsion through a fine channel at approximately 6000 psi. Turbulence in the interac-

tion chamber produces fine particles in normal emulsions. However, the turbulence caused our emulsions to break. With some redesign of the orifice and interaction chamber, this apparatus may be able to refine our emulsions. The third pumping technique uses a peristaltic pump to force the emulsion through fine tubing. The shear with the wall of the tubing caused the emulsion to become finer. This led to an increase in emulsion viscosity, and to phase separation in current apparatus designs. Dilution in the pump is also difficult, and both air and nonuniformities can be introduced.

The main disadvantage of all these techniques is that density variations throughout the emulsion are difficult to remove because little random mixing occurs. Hence, if the water is not metered precisely into the emulsion and a density variation exists, this variation is maintained and is not eliminated by mixing with adjacent volumes of emulsion. This is a problem common to all pumping techniques. We envision a hybrid mixing technique in which a uniform crude emulsion is first prepared by stirring and is then refined by using a high-shear pumping technique.

Interfacial Tension Measurement

Because of the energy required to create the large surface areas in emulsions, thermodynamics demands that they break eventually. However, metastable emulsions may be made by proper balancing of stabilizing and destabilizing forces. Destabilizing forces include the interfacial tension, which is the work per unit area required to create an interface; long-range van der Waals forces; and pressure differences in the interfacial film, which lead to drainage (also called border suction from Plateau borders).

Stabilizing forces mainly arise from the use of a surfactant, or emulsifier. In our systems, a surfactant has a lipophilic (oil-loving) and a hydrophilic (water-loving) end; this results in strong attractive forces for the surfactant at the interface. In addition, the presence of the surfactant in the bulk of the oil disrupts the order of this phase. Thus, the surfactant preferentially exists at the interface, lowering the interfacial tension. The shape of the surfactant at the interface can lend itself to stabilization by steric forces. Film elasticity, arising from the Gibbs and Marangoni effects, is another stabilizing force that is ascribed to the surfactant. The last major stabilizing forces are electrostatic, where the presence of an ionic species can induce an electric double layer at the interface.

Most of these effects are difficult to observe directly. The interfacial tension, however, may be measured by many techniques. This force may also be the most important since without a low interfacial tension an emulsion cannot be made at all. Therefore, we measured interfacial tensions of our styrene/DVB/water systems as a function of the percentage of Span 80, surfactant type, styrene/DVB ratio, and presence of electrostatic agent, $AlCl_3$, in the water phase.

Two methods were used to measure the interfacial tension in our two-phase systems. In the pendant drop method, the interfacial tension is determined from the shape factors of a drop of the oil/surfactant phase suspended in the water phase. In the ring tensiometer method, the interfacial tension is related to the force required to pull a platinum ring through the interface.

Figure 4 shows the interfacial tension as a function of surfactant concentrations ranging from 0 to 10 wt/vol%. The interfacial tension drops rapidly from its initial value of 17 dyn/cm (by the ring tensiometer method) or 30 dyn/cm (by the pendant drop method) to 4 to 5 dyn/cm by 0.5 wt/vol%. Above this concentration, no further reduction in interfacial surface tension is obtained. This shows that the critical micellization concentration is reached by 0.5 wt/vol% of Span 80. This result is consistent with the conclusion drawn from analyses of Brunauer-Emmett-Teller

(BET) data and density that an amount of Span 80 equal to 1 wt% of the oil phase is adequate to form a single monolayer of surfactant. Indeed, emulsions can also be made with this amount; however, they are unstable. In fact, we find that stability is continuously improved as the amount of Span 80 increases up to 20 wt% of the oil phase. We do not yet know what role the additional Span 80 plays in stability.

As discussed above, the difference between the ring tensiometer and pendant drop interfacial tension measurements is virtually gone at 1 wt/vol% Span 80, and may be due to time allowed for equilibrium. The trends and the point of monolayer formation are the same for both techniques, so the conclusions seem justified.

Using the ring tensiometer, we found no significant effect on interfacial tension of the styrene-to-DVB² ratio.

We also measured the interfacial tension of three additional surfactant-in-oil/water interfaces using the ring tensiometer. We tried barium and calcium oleate, and magnesium stearate at about 9 wt% (which is estimated to be ~10 wt/vol%) in styrene/DVB (40/60). As can be seen in Fig. 4, the interfacial tensions of these systems ranged from 12 to 14 dyn/cm, far greater than the value of 5 to 6 dyn/cm for Span 80 at the same concentration. This is consistent with the emulsion stability results described above.

Figure 4. Interfacial tension as a function of surfactant concentration and type.

As mentioned above, we found that addition of AlCl_3 improved the emulsion stability significantly. However, the interfacial tension was not found to change when measured by the ring tensiometer method.

The major finding of this study is that Span 80 at 0.5 wt/vol% or greater in styrene/DVB gives the lowest interfacial tension of the surfactants we tested. We also concluded that the styrene/DVB ratio and the concentration of AlCl_3 in the water phase have no effect on the interfacial tension under equilibrium conditions.

Theoretical Study

We initiated a theoretical study of emulsion stability to determine if the ability to achieve a small cell size and a high volume fraction of water (vfw), and thus a foam of density roughly equal to the volume fraction of oil (vfo), may be limited by certain geometric constraints. There are two cases to consider: spherical and nonspherical droplets. Certainly as the emulsion begins to form and the vfw is still low, the water droplets will be spherical so as to minimize the interfacial energy.

Our SEM results show that in the final HIPE both spherical droplets and polyhedral droplets with distinctly flat sides can occur, depending on how the emulsion is prepared and on the degree of coalescence. To probe the geometrical constraints, we examined both spherical and polyhedral structures.

The spherical droplet case is in some respects the more complex. One can note first that to reach a high vfw, one must have a distribution of droplet sizes. This is because droplets of the same size, regardless of their diameter, can only be packed to a vfw equal to 0.74, the close-packed volume fraction. We first consider how a distribution of droplets might pack to fill the available space most efficiently. Any real distribution would of course pack less efficiently, and thus reduce the vfw.

Our approach is as follows. We start with a cubic-close-packed (ccp) arrangement of monodisperse spheres, perhaps most simply represented by the face-centered-cubic (fcc) unit cell. These primary spheres will set the scale for our lattice and will represent the largest cells in the final foam structure. The vfw here is 0.74. The largest voids in this lattice are the octahedral holes. In these holes, we can place particles with a diameter equal to 41% of the diameter of the primary spheres. The next largest voids are the tetrahedral holes, which accommodate even smaller particles. If we fill these and then continue in this fashion, always filling the largest voids, we will

continue to add smaller and smaller spheres and can obtain whatever vfw is desired, independent of the size of the largest spheres.

Unfortunately, nature places two constraints on this model for real materials. First, if the spheres are to represent water droplets, there will be some minimum size possible because of the curvature of the small droplets and the increasing amount of work necessary to divide already small droplets into smaller ones. Having a minimum-sized droplet means that the obtainable vfw is limited. More importantly, the vfw depends on the size of the primary spheres in the system in such a way that the smaller the primary spheres, the lower the vfw. The second constraint is that there must be some finite interfacial oil thickness between the droplets to prevent them from coalescing. The effect of this constraint on the vfw is again to reduce it, and the effect is more pronounced for systems with smaller primary spheres.

Using a computer, we started with an fcc unit cell as described above and filled voids until the size of the smallest spheres being added was about 1/100th the diameter of the primary spheres. At this point, more than 20,000 spheres of decreasing size have been placed in the voids of the fcc unit cell.

We then looked at the vfo (which is approximately equal to the true density in g/cm^3) as a function of the size of the primary spheres, of the size of the smallest spheres included, and of the interfacial thickness w (which has the effect of reducing the radius of each sphere by $w/2$). The results of our calculations are displayed in Fig. 5. The three sets of lines shown are for systems with primary sphere diameters of 1, 3, and 5 μm . The three lines in each set correspond, from bottom to top in each group, to values of w equal to 0, 7.5, and 15 nm. Note first the bottom line ($w = 0$) in each group. All of these lines will extend to zero vfo as the radius of the smallest particle approaches zero. For nonzero w , the constraint of the size of the primary spheres can be clearly seen. For the system with primary spheres of diameters of 1 μm and $w = 15$ nm, the minimum vfo that can be achieved is about 0.17; an interfacial thickness of 7.5 nm would give a vfo of between 0.11 and 0.12. It is clear that a maximum cell size of 1 μm and a vfo of 0.05 can only be simultaneously obtained for interfacial thicknesses that are very small, probably in the range of 1 to 2 nm. The situation is clearly worse if we also require a minimum droplet size.

For the foams prepared so far, the smallest maximum cell size obtained is about 3 μm , with

Figure 5. Volume fraction of oil as a function of primary sphere size, size of smallest spheres, and interfacial thickness w .

densities of about 0.05 g/cm^3 . This value is consistent with our calculations if an interfacial thickness of 5 to 7.5 nm is required.

Although the above results are based on an ideal system that starts with a perfect ccp arrangement of spheres, it is unlikely that the results are particularly sensitive to this condition, which was used for convenience. It is likely that this arrangement is the most efficient packing of the distribution of spheres and that it sets very precise requirements on the distribution of sizes allowed, particularly for the largest spheres. But by the time the radius of the spheres being added in the $w = 0$ case has dropped to 1/10 of that of the largest spheres, only 171 spheres have been used and

the v/o is 0.17. More than 20,000 additional spheres are added before the radius of the spheres has dropped by another 1/10 and the v/o is now only slightly less than 0.05. Although these smaller spheres are certainly packed in an organized way, their distribution of sizes is nearly continuous. Further, numerous studies on the random packing of monodisperse spheres have shown that the difference in packing fraction from the ccp system is about 10%, suggesting that our results for spheres, though representing an ideal case, may not be too far from what one would get for a random packing of a broad distribution of particles.

The previous discussion has been for spherical droplets. As noted earlier, some of the micrographs show polyhedral droplets (see Figs. 1 and 2). The relationship among density, interfacial thickness, and cell size is in many ways simpler for polyhedra than for spheres. One important feature is that consideration of a distribution of polyhedral sizes is no longer necessary. If we let d be some measure of the diameter of the polyhedron, then the volume of the polyhedron is some constant times d^3 . If we again let w be the interfacial thickness, and we include one-half of that thickness in the representative polyhedron under consideration, then in the limit $w \ll d$ the vfo would be $3w/d$. For example, if we wanted our cell size to be $1\ \mu\text{m}$ and the density to be $\sim 0.05\ \text{g/cm}^3$, the interfacial thickness would have to be $16.7\ \text{nm}$, clearly a less stringent requirement than that necessary for spheres. However, it must be remembered that this represents an upper limit. Any curvature in the interfacial region, thickening in the region of the vertices, or polydispersity will rapidly reduce this allowed thickness toward zero, thus breaking the emulsion.

In conclusion, we can note that the geometric considerations coupled with the physical properties of the materials set reasonably well-defined limits on the obtainable material densities for a given maximum cell size. Even with the best surfactants it seems unlikely that we can form stable emulsions with interfacial thicknesses of less than about $5\ \text{nm}$ without rapid membrane rupture and coalescence to larger cells. At a desired density of $0.05\ \text{g/cm}^3$ this would allow for polyhedral cells of about $0.3\text{-}\mu\text{m}$ diam in the ideal case and probably 2 to 3 times this for a real system, and it would allow for spherical cells of about $1\text{-}\mu\text{m}$ diameter.

Foam Performance

Specifications

The foam we are making will be used to hold liquid-DT in a spherical shell configuration. To perform this task the material must meet certain specifications, which arise from both target physics and liquid-wetting stability constraints. To meet the target physical requirements, the foam should have a density of $0.05\ \text{g/cm}^3$, a $1\text{-}\mu\text{m}$ pore size, a minimum of higher- Z contaminants, and uniformity of better than 1% in $30\text{-}\mu\text{m}$ -diam cores through the foam. The PS foams we are making have both cells and pores. The cell size affects the uniformity of the foam; the pore size affects the

wetting. To hold the liquid-DT stably, the pore size must be on the order of $1\ \mu\text{m}$.

We use a wide range of characterization techniques to guide us in foam development and to verify the specifications. To measure cell size and pore size, we use primarily SEM, but BET analysis of nitrogen adsorption data provides a bulk average analysis that helps confirm the accuracy of the SEM data. We also use mercury intrusion porosimetry to measure the pore size. We find x-ray radiography to be very useful for measuring the uniformity because it shows the presence of voids and density variations. Density is measured by weighing samples of known volume. Other comparative physical measurements are needed to assess progress in foam formulation and to provide engineering data for target construction. The main engineering data we are interested in are foam machinability, the compressive modulus and thermal expansion coefficient, and structure and wetting properties, which are discussed below.

Foam Properties

Machining is necessary in the production of both final target geometries and regularly shaped samples for characterization. Using specially modified milling machines—one machine with a rotary saw for a cutting head and the other with a vibratome—we cut samples for further testing at LLNL. The samples are roughly shaped with the rotary saw and cut to final dimensions and surface finishes with the vibratome.

Mechanical and thermal properties are important because the foam must be machined into a shell and cooled to $20\ \text{K}$. We determined compressive moduli of PS foams by analysis of stress-strain curves. The stress-strain curves were obtained using a mechanical testing machine to compress the sample to a 4% maximum strain at $0.1\ \text{mm/min}$. In all cases, the strain rate was a constant $1\%/min$ or less.

As shown in Fig. 6, the compressive modulus of PS foams increases with increasing density from about $10\ \text{MPa}$ at $55\ \text{mg/cm}^3$ to about $21\ \text{MPa}$ at $106\ \text{mg/cm}^3$. For comparison, we used the model of Ashby⁶ to predict compressive moduli of open-celled PS foams. There is reasonable agreement between the predicted values of the model and those observed, at least in this density region. Figure 6 also shows the compressive moduli of PS foams made by our group and by Unilever in 1985. At $106\ \text{mg/cm}^3$ density, our current material shows a twofold improvement in compressive strength compared with the 1985 material. When compared with the Unilever material at $70\ \text{mg/cm}^3$

Figure 6. Compressive modulus as a function of foam density and aspect ratios.

density, there is a similar improvement. We attribute this improvement to the homogeneity achieved by the syringe-pump method.

Modulus values for two additional types of foams are also shown in Fig. 6. At a density of 65 mg/cm³, a PE foam has a value of 2 MPa, while silica aerogel has a value of less than 2 MPa at a density of 75 mg/cm³ and a value of about 5 MPa at a density of 109 mg/cm³. Clearly the current PS foams are superior in compressive strength.

The coefficient of thermal expansion (CTE) between room temperature and 20 K was measured on a thermal mechanical analyzer. The CTE was determined to be 5.6×10^{-5} cm/(cm·K) for a PS foam sample of 65 mg/cm³ density. The CTE for full-density PS is 6 to 8×10^{-5} cm/(cm·K). This corresponds to a 1.5% linear shrinkage in foam cooled from room temperature to 20 K. For comparison, silica aerogel shows no shrinkage or a slight expansion over the same temperature range.

The structure of the PS foams is important both for target physics and wetting physics. We

primarily use the SEM to characterize foam structure, although BET and mercury intrusion porosimetry are also used. We relied on x-ray radiography to assess the foam uniformity. Recently, we investigated an optical densitometry technique that may also help in measuring foam uniformity.

Figure 1(b) shows the microstructure of one of our best foams, which was made by the syringe pump method. The cell size is less than 3 μ m; pore diameters are less than 1 μ m. Figure 7 compares a radiograph of a uniform foam with one of a nonuniform foam. In the nonuniform foam, bubbles are visible in addition to density gradients caused by incomplete mixing. The uniform foam has no bubbles and demonstrates excellent uniformity except for a thin region in contact with the mold, which is higher density. We do not yet have the ability to quantify the density uniformity from the radiograph. However, the addition of image analysis equipment to our target characterization facilities, coupled with the Laser Experiments Analysis Facility, will soon give us the ability to measure density uniformity.

(a)

(b)

Figure 7. X-ray radiographs showing foam uniformity:
(a) uniform foam; (b) nonuniform foam with bubbles.

Unilever Research, which originated the inverse emulsion foam concept, has a contract with LLNL to provide foam material as well as to help develop improved material. Figure 8 shows the microstructure of the material they made for us in 1986, which has a cell size of approximately $5\ \mu\text{m}$ and a pore size of 1 to $2\ \mu\text{m}$. Figure 9 shows radiographs of two foam rods with moderately good uniformity. However, some bubbles are visible as well as regions of high density. Approximately 10% of the foam sample merits examination as target-quality material.

Foam Wetting

Polymer foams used in laser fusion targets must be wetted with liquid DT. To help understand the dynamics of wetting, we used other liquids such as ethanol or hexane, which do not pose cryogenic handling problems, or hydrogen, which does not pose a radiation hazard. The rate of wetting and the capillary pressure were measured. The following discussion of the results is taken from Ref. 7.

To interpret the wetting measurements, the physics of foam wetting must be understood.

Wetting of foams with a pore radius r by a liquid with surface tension γ and contact angle θ is driven by the capillary pressure, which is given by the Young-Laplace equation:

$$\Delta P_c = \frac{2\gamma \cos \theta}{r} \quad (1)$$

If we assume that the wetting of foams is similar to the wetting of an array of capillary tubes, we can determine the equilibrium height to which liquid rises in the foam as follows:

$$h_e = \frac{2\gamma \cos \theta}{rg\rho} \quad (2)$$

where g is the acceleration due to gravity and ρ is the density of the liquid. For ethanol and hexane the capillary height is approximately 280 cm, assuming a zero contact angle and a $2\text{-}\mu\text{m}$ -diam pore size. The rate of liquid flow in tubes is related to the pressure driving force by the Poiseuille equation:

$$\frac{dh}{dt} = \frac{r^2 \Delta P}{8\mu h} \quad (3)$$

Figure 8. Scanning electron micrograph of a Unilever foam with 5- μ m cell size.

where μ is the viscosity of the liquid. The pressure driving force [Eq. (1)] can be substituted into Eq. (3) to give the rate of movement of the interface:

$$\frac{dh}{dt} = \frac{r \gamma \cos \theta}{4\mu t} \quad (4)$$

Equation (4) is then integrated to solve for the position of the interface during initial wetting:

$$h = \sqrt{\frac{r \gamma \cos \theta t}{2\mu}} \quad (5)$$

To follow the wetting of ethanol, we weighed a piece of foam just touching the surface of the liquid. As the ethanol wicked into the foam, the height increased as shown in Fig. 10. The results for PE foams are shown for comparison. The wetting behavior of the two foams is very different. The PE foam with a density of 0.048 g/cm³ wicked to a height of 0.6 cm in 100 min. After ~1000 min, a height of 2.4 cm was reached, which is far short of the capillary height. The PS foam with a density of 0.081 g/cm³ wicked to a height of 4.8 cm in 100 min, nearly an order of magnitude more than the PE foam. We believe the PE foam wetted so slowly because of a nearly 90° contact angle or a nearly closed cell structure in the PE foam. In addition, since wetting was so slow, we believe that surface evaporation from the PE foam is the reason the predicted capillary height was not reached.

The critical surface tension is 31 dyn/cm for PE and 33 dyn/cm for PS. This small difference in surface energy does not explain the difference in wetting behavior. When the emulsion is made, a surfactant is used to stabilize the inverse emulsion. The hydrophilic groups are adsorbed on the water droplets. When the water is evaporated, the surfactant is left behind at the interface and its hydrophobic groups may dissolve in the polymer. This would leave an interface composed not of PS but of higher-surface-energy groups, which may increase the wetting rate.

We measured the pressure required to force an organic liquid from the foams. The foam is

Figure 9. X-ray radiographs of Unilever foams showing bubbles and high-density regions.

Figure 10. Ethanol wetting of PS and PE foams.

bonded to a tube and then touched to the surface of the liquid. Sufficient time is allowed to elapse for complete wicking. The filled foam is then submerged just below the liquid surface. Gas pressure is slowly increased to the tube that is connected to flow sensing apparatus. At the capillary pressure [given by Eq. (1)], gas begins to flow and visible bubbles emerge from the foam. The capillary radius was calculated from measurements of this bubble-point pressure. The PS foams were found to have a capillary radius of approximately $2\ \mu\text{m}$. This technique provides a measurement of the stability of the liquid fill to applied pressure.

Figure 11 shows wetting of PE and PS foams by liquid hydrogen. Again the PE wicks the liquid slower than the PS foam. In the case of hydrogen wetting, the contact angle is essentially zero. From Eq. (4) the rate of wetting must then be determined by the pore radius. This would imply that the pores in this PE sample are smaller than the cells visible on the scanning electron micrograph. Figure 12 shows the wetting data plotted accord-

Figure 11. Liquid hydrogen wetting of PS and PE foams.

ing to Eq. (4). The pore radius r was $0.17\ \mu\text{m}$ for PS foam and $0.0045\ \mu\text{m}$ for PE foam. The small pore size explains the slow wetting of PE foam.

Conclusion

Polystyrene foam development has progressed to the point where we can make foams that meet many of the target requirements. The emulsion chemistry, which was developed from the Unilever process and our best syringe-pump mixing method, is capable of producing uniform 2- to $3\text{-}\mu\text{m}$ cell size and $1\text{-}\mu\text{m}$ pore size foam with a density of $0.05\ \text{g/cm}^3$. Our foams show an improvement in uniformity and compressive moduli over those of Unilever. The foams perform well with respect to liquid hydrogen wetting. We increased our understanding of some of the fundamental properties affecting emulsion stability, although there are several unanswered questions.

In 1987, we will focus on optimizing PS foam preparation and determining key variables and how they control the process. We will continue to increase our understanding of the emulsion system, and we will develop techniques to ensure that the foams meet the remaining target requirements.

Figure 12. Analysis of liquid hydrogen wetting experiments to determine foam pore size.

Resorcinol-Formaldehyde Foams

Introduction

Resorcinol-formaldehyde (RF) foams hold promise for DT-fill stability in target shells because of their extremely small cell size. In 1986, we made foams from 100 to 200 mg/cm³ in density, with about 0.1-μm cell size, as shown in Fig. 13. The foams are brittle and are dark red-brown in color. Preliminary tests showed they can be wetted with liquid H₂ and machined on a rotary saw without producing visual fractures.

Resorcinol-formaldehyde foams were developed in 1986 by R. Pekala at LLNL. The procedure is based on the one used for RF or phenolic adhesives, which were favored in World War II because of their durability, low cure temperature, and high strength bonds to many materials.⁸ The major differences in the procedure for making foams are a lower percentage of reactants to achieve desired densities, a higher ratio of formaldehyde to resorcinol to increase cross-link density (2:1 as compared to about 1:1 in the adhesives), and the drying steps.

Standard Procedure

The standard formulation for RF is 6 wt% reactants in water. Resorcinol and formaldehyde in a 1:2 molar ratio, respectively, are combined with 0.2 wt% initiator (sodium carbonate). The mixture is stirred at 60°C for 2 h, and then sealed in an ampule to gel at 80°C for 2 to 7 days. We then dry the gels in a series of exchanges. First, the water is exchanged for methanol, then the methanol is exchanged for amyl acetate, and finally, the amyl acetate is exchanged for liquid CO₂. Each exchange takes about 5 days under static conditions. The CO₂ is taken above its critical temperature and is bled off to avoid passing a liquid meniscus through the material.

Parameter Studies

We investigated the effects of some formulation and process changes on the gel and foam. In the formulation, we varied the composition of the

Figure 13. Scanning electron micrograph of RF foam with cell sizes of 0.1 to 0.2 μm .

solvent, reactants, and initiator. We also changed stir time and temperature, and cure time and temperature, in the process variables. Success of the changes was largely measured by whether or not the samples gelled. We measured the solvent swelling in methanol of some sample sets. The volume change in swelling indicates how tightly the gels are cross-linked.

The solvent was varied from 100% water to 100% methanol to see if we could eliminate the first exchange step and thereby cut the drying time in half. All samples gelled within 48 h or less. Solvent swelling in methanol showed that samples that were gelled in 100% water were more tightly cross-linked. As the ratio of methanol to water increased in the reaction solvent, the samples tended to burst and become mushy during solvent swelling, indicating very low cross-linking.

We also replaced resorcinol with phloroglucinol, which has three hydroxyls compared with resorcinol's two. The three active sites between the hydroxyls are equally reactive in phloroglucinol, increasing the likelihood of getting a trifunctional cross-link. Air-drying of phloroglucinol/formaldehyde gels resulted in only about 20% shrinkage, promising perhaps none in super-critical extraction.

We are in the early stages of process-variable screening tests, where we chose extreme values of eight variables:

- Ratio of R:F was 1:1 or 1:3.
- Percentage of reactants was 3 or 12 wt%.
- Initiator concentration was 0.05 or 1.0 wt%.
- Stir time was 0.5 or 4 h.
- Stir temperature was 40 or 70°C.
- Cure time was 1 or 7 days.
- Cure temperature was 60 or 120°C.
- Samples were cooled either quickly in air or slowly in a bath.

This experiment is described in more detail in the section "Experimental Design for Foam Optimization." It appears that gelation depends most strongly on the ratio of R:F and initiator concentration, where 1:3 and/or 0.05% are the values most likely to result in gelation. We will do compression testing of the samples that gelled and compare molecular weights between cross-links. The gels will be dried, and structures seen by SEM will be compared.

Properties and Specifications

We are interested in achieving the most uniform and complete network structure possible to increase the uniformity and strength of the finished foam. Therefore, we are measuring the average molecular weight between cross-links, $\bar{M}_c$, of the gels by analysis of compression testing. We also used the data from differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) to determine the thermal stability of the foam and help us determine if curing is complete. The final structure of the foam is examined using SEM and BET surface-area analysis of N_2 absorption.

To obtain the data for the determination of $\bar{M}_c$, we compressed a cylinder of gel to 1% strain. From the slope of the stress-strain curve, we determined the compressive modulus to be 0.019 MPa. $\bar{M}_c$ was then found to be 79,000. This value corresponds to about 670 repeating units between cross-links, where one possible repeat unit is as shown in Fig. 14. This is a low degree of cross-linking, and may explain problems we have with shrinkage during extraction.

Figure 14. One of the possible repeat units between cross-links of RF.

We analyzed a foam sample using DSC and TGA. Both scans indicated solvent loss between room temperature and about 140°C, followed by an exothermic reaction where the sample lost weight from about 200 to 400°C. The weight loss is probably the result of curing, with water formed in the condensation reaction and lost during heating. If the sample is continuing to cure, this result is consistent with the low degree of cross-linking found from compression tests, and indicates that application of heat may increase the degree of cure.

Figure 13 shows a scanning electron micrograph of an RF foam with a density of 130 mg/cm³.

The structure looks like tiny balls about 25 nm in diameter, strung together to form interconnected fibers. The cell sizes range from about 0.1 to 0.2 μm. As one would expect, the foams have a very high surface area, 640 m²/g as determined from BET surface-area analysis.

We sent an irregular piece of RF foam to the National Bureau of Standards for wetting tests identical to those described for PS foam in the preceding section. The sample wetted readily and completely with liquid H₂. We also determined that foams cut with a rotary saw had no visible fractures.

The density of a finished foam is not predictable, ranging from 100 to 200 mg/cm³, with at least 20% shrinkage. The cause of the shrinkage may be incomplete curing or some part of the exchange and extraction process. We are trying several approaches to determine the cause of the shrinkage. One is to dry the material by direct supercritical extraction of the water. This requires a temperature greater than 370°C and a pressure of 3000 psi, but it eliminates the 2- to 3-week solvent exchanges. Another approach is to increase the stiffness of the gel, either by increasing the degree of cure, or by using a different molecule, such as phloroglucinol, to increase the number of possible cross-link junctions.

Because of their wetting characteristics, the RF foams may have advantages over larger-celled foams. We are working to solve the problem of shrinkage during drying by improving the cross-linking in the gel and/or by drying in a different fashion.

Experimental Design for Foam Optimization

Introduction

We are applying the principles of statistical experimental design to the development of PS and RF foams. This methodology is a useful supplement to more classical kinds of experimentation. It allows for identification of key variables within a system, which leads to better control of processes, and it provides a means of optimizing the system with respect to those variables. It also increases the efficiency of experimental development by minimizing the number of experiments and by organizing the data in computer programs that can predict results.

Statistical Experimental Design

The application of basic statistical principles to experimental design is a well-developed methodology.^{9,10} Although at first glance this statistical approach may appear to be contradictory to the principles of classical experimentation, in fact the two approaches are complementary and are appropriate at different stages in the development of a product or process. To choose between the two, we need to understand the basic ideas behind each approach.

Classical experimentation, which is also called "one-factor-at-a-time" experimentation, is

designed to look at only one independent variable (x) in the system of any given experiment and to measure the response (y) of the system to changes in this variable. This strategy assumes that:

- The response is likely to be a complicated function of any one x with various bumps and kinks over the experimental range. This requires many experimental levels for each variable.
- The effect of any other x is simply to raise or lower the function but not to change its shape or slope. In other words, interactions between independent variables are negligible.
- The experimental error is negligible compared with the effects of the x 's.

Statistical design starts from a process that is operable most of the time, but which is far from optimized, and proceeds through well-defined stages. The first stage is called a screening experiment and identifies the key variables in the process. The second stage, response surface methodology (RSM), develops prediction equations within the range of variables covered. The third stage is development of a theoretical model, which is necessary if extrapolation (for example, scaleup) of the process is required. We discuss only the first two stages here. Statistical design assumes that:

- Over the experimental range, most response functions are smooth, with perhaps an upward or a downward curvature.
- The slope or shape of a response function may change significantly when the levels of other x 's are changed. In other words, interactions are typical.
- The experimental error is not negligible compared with the effects of the x 's, and it may contain both bias and random components.

Because these two experimental approaches—classical and statistical—contain such different assumptions, it is obvious that use of one to the exclusion of the other could lead to very misleading results, since it is not known at the outset of a development which set of assumptions is valid. In practice, the greatest danger in using only the "one-factor-at-a-time" approach is the neglect of interaction terms.

Normally, the classical approach is needed at the beginning of a development when virtually nothing is known about the system, and it is necessary to identify potential key variables and the ranges of those variables over which the system will function. At some point, however, enough information will have been gathered to enable the experimenter to initiate a statistical experiment, and from this point this approach is generally more efficient and yields more useful results. The

greatest danger in the use of the statistical approach lies in not paying strict attention to the statistical calculations that tell the experimenter whether the underlying assumptions used in the design are valid.

All of the statistical designs that we discuss are called factorial designs and are based on the concept of factor space. The designs permit *simultaneous* estimation of the effects of several factors. Both main effects and interactions are estimated. For a system with p factors and m levels for each factor, the factor space is completely defined with $n = m^p$ experimental runs. Normally, because the number of experiments is too large, the full factorial designs are not run. Instead, various types of fractional factorial designs are used. (The terms factor and independent variable are equivalent.)

Screening Experiments

The first stage in statistical design is called a screening experiment. Because the number of experimental runs needed to optimize a system depends exponentially on the number of factors, it is important to keep this number to a minimum. This is done by listing all potential factors, and setting a high and low level for each. The factors are then varied throughout the levels in a statistical pattern. Several designs are available, including those developed by Plackett and Burman¹¹ and fractional-factorial designs. The specific choice depends on the details of the system being studied and on the number of runs required for the different alternatives. For eight variables, the design of choice is a fractional factorial that requires 16 runs. After measuring the desired responses for the different runs, a statistical calculation is performed that gives the factor effects for each factor and the minimum significant factor effect. If a specific factor effect exceeds the minimum significant effect, then that factor is judged to be a key variable within the confidence limits of the statistics. As with all statistical designs, the runs are executed in random order to minimize bias errors. Since screening designs are two-level designs containing a fraction of the factor space, they give only limited information about curvature of the responses or about interactions. To estimate these, one proceeds to the RSM stage.

Response Surface Methodology

In a response surface design, fractional factorial designs are also used, but they are at least three-level designs, so curvature and interaction effects may be determined. When greater accuracy is needed, five-level designs are used, but this

greatly increases the number of required runs. The basic approach is the same as for the screening study: the factors are selected (presumably the ones identified as key variables in a previous screening experiment), the levels are determined, and a specific design is selected. Probably the most common response surface design is the three-level Box-Behnken type.¹² With three key variables, the experimental points lie at the center of a cube and at the midpoints of its 12 edges. The cube's center point is replicated three times (yielding an estimate of reproducibility), for a total of 15 runs. The number of runs per key variable is greater for an RSM than for a screening study: a screening study of eight variables requires only 16 runs. It is thus clearly important to determine the key variables before proceeding to the response surface stage. It is also desirable in an RSM to identify those variables that are related to the formulation of the product, and those that are related to the process for making it, and to deal with them separately.

The statistical analysis of a response surface design allows one to determine an empirical model for each response as a function of the factors. To do this, a model type must be chosen. The most common choice is to model the responses as quadratic polynomials, where the coefficients of the various terms are determined by a linear least-squares regression. For the three-factor case, the equation for any response y_i would be

$$y_i = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3, \quad (6)$$

where the b 's are the coefficients that give the best fit between the terms in the equation and the observed values of that particular response.

This analysis is done on a computer, which can then plot contour maps of the response surfaces for any combination of factors. The regression equation can also be used to calculate responses for any values of the variables within the factor space of the experiment. A variety of estimates of the goodness-of-fit and other statistical parameters are also calculated, and different model types can be used if the data indicate this is appropriate. In all statistical designs, it is important to make the experimental ranges as wide as possible to ensure that key effects will not be missed. The results *cannot* be extrapolated.

Applications to Foam Development

Based on the results of the experimentation described in the previous sections, we assessed the status of foam development for the PS and RF systems. Using this analysis, we designed experiments that employ the statistical principles described above.

For PS foams, the variables fall fairly neatly into formulation and process categories. Experiments indicate that the ratio of styrene to divinylbenzene, the concentration of initiator, and the concentration of surfactant all have an effect on important foam properties. These are all formulation variables, and enough classical experimentation has been done to determine over what

Table 1. Three-variable Box-Behnken design for PS foams. Fixed parameters: (1) batch size: 25 g; (2) target density: 0.050 g/cm³.

Design run No. ^a	x_1	x_2	x_3
1	100	1.5	22.5
2	100	0.1	22.5
3	0	1.5	22.5
4	0	0.1	22.5
5	100	0.8	35.0
6	100	0.8	10.0
7	0	0.8	35.0
8	0	0.8	10.0
9	50	1.5	35.0
10	50	1.5	10.0
11	50	0.1	35.0
12	50	0.1	10.0
13	50	0.8	22.5
14	50	0.8	22.5
15	50	0.8	22.5

Factor	Range
x_1 = % styrene	0-100% of monomer ^b
x_2 = % initiator ^c	0.1-1.5 wt% of the water phase
x_3 = % surfactant ^d	10-35 wt% of oil phase

Response	
y_1 = emulsion droplet size	y_5 = density uniformity
y_2 = foam cell size	y_6 = BET surface area
y_3 = foam pore size	y_7 = hexane wetting rate
y_4 = density	y_8 = compressive modulus

^a This sequence refers to the design only; experiments are performed in random order.
^b Remainder is divinylbenzene.
^c Sodium persulfate.
^d Span 80 (sorbitan monooleate).

Table 2. Fractional-factorial screening design for RF foams.

x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8
0.05	5	1:1	High	4	70	1	120
1	5	1:1	Low	0.5	70	7	120
0.05	15	1:1	Low	4	40	7	120
1	15	1:1	High	0.5	40	1	120
0.05	5	3:1	High	0.5	40	7	120
1	5	3:1	Low	4	40	1	120
0.05	15	3:1	Low	0.5	70	1	120
1	15	3:1	High	4	70	7	120
1	15	3:1	Low	0.5	40	7	60
0.05	15	3:1	High	4	40	1	60
1	5	3:1	High	0.5	70	1	60
0.05	5	3:1	Low	4	70	7	60
1	15	1:1	Low	4	70	1	60
0.05	15	1:1	High	0.5	70	7	60
1	5	1:1	High	4	40	7	60
0.05	5	1:1	Low	0.5	40	1	60

Factor	Low value	High value
x_1 = wt% of initiator	0.05	1.0
x_2 = wt% of reactants in solvent	5.0	15.0
x_3 = molar ratio of F:R	1:1	3:1
x_4 = cooling rate	Low	High
x_5 = stirring time (h)	0.5	4
x_6 = stirring temperature (°C)	40	70
x_7 = time in oven (days)	1	7
x_8 = oven temperature (°C)	60	120

Response	
y_1	= gel formed or not
y_2	= degree of cross-linking
y_3	= density of dry material
y_4	= cell size

range of each variable foams can be made successfully. Several processes work reasonably well; the one that uses the syringe-pump as the mixing method seems to give the best overall results.

On the basis of this assessment, we designed a three-variable, formulation response surface experiment that will optimize the system with respect to several responses. The design details and a list of the responses selected are shown in Table 1.

The responses chosen all relate to important foam properties. We believe that y_1 , the emulsion droplet size, determines y_2 , the cell size in the resultant foam, and we wish to determine whether this is true over this range of formulations. The foam pore size y_3 should determine the wetting rate y_7 so these responses should be correlated, and y_6 , the BET surface area, should be related to these two as well. The density y_4 and density uniformity y_5 are critical to the foam's performance as a target, and y_8 , the compressive modulus, determines the mechanical properties of the foam. We

should have enough material from each formulation to measure these eight responses.

For this experiment, all the process parameters will be fixed at those used in the syringe-pump method. Once this optimization is complete, the process parameters will be studied separately.

For the RF system, the development of the process is not as far advanced, and there is no clear indication of the relative importance of formulation and process variables. A number of factors in both categories are believed to affect foam properties, but it is not yet known which of these factors is significant. Therefore, it is appropriate in this case to execute a screening experiment to identify these key variables.

The design that we developed, shown in Table 2, is a fractional-factorial type that uses eight variables. Of the potential key variables chosen, the first three are formulation variables relating to the chemistry of the system. The initiator used is sodium carbonate, so x_1 also determines the pH. The

solvent used is water. The last five variables are related to the process of making the foams. The responses are fewer in number than for the PS experiment, which is more typical of a screening study where the object is simply to determine

which variables to pursue further. Once these variables are identified, an optimization process similar to the one described for the PS system can proceed.

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