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Low-Density Hydrocarbon Foams for Laser Fusion Targets

Progress Report—1987

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Abstract

This report describes progress made in the development of direct-drive hydrocarbon foam targets for laser inertial confinement fusion during 1987. The foam materials are polystyrene, resorcinol-formaldehyde, carbonized resorcinol-formaldehyde, and cellulose acetate. The processes for making the foams, their properties, characterization techniques, and the relationship of their properties to target specifications are presented. Progress in the creation and testing of prototype targets is also described.

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Introduction

We are developing foams for the direct-drive, high-gain, inertial confinement fusion (ICF) target that is described in the *Laser Program Annual Report 85*¹ and in a paper by Sacks and Darling.² This target design calls for a spherical shell of foam that can be wetted with liquid deuterium-tritium (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 laser energy.

The foam should have a density of 50 mg/cm³ or less 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 4 μm to meet uniformity requirements, and a pore size of less than 1 μm to stably hold the liquid DT. The foam must be machinable or moldable to the required spherical-shell configuration and tolerances. The foam must tolerate exposure to the radiation environment of tritium and to cryogenic temperatures without changing dimensions during the time needed for the target to fill and stabilize before a shot. Some target designs will require a foam with an overcoat of approximately 5 μm of a hydrocarbon or other low-*Z* material.

In 1986, two foam materials were under development: polystyrene (PS) foams made from an inverse emulsion system, and resorcinol-formaldehyde (RF) foams made from condensation polymerization gels. Our work in 1987 continued the development of these foams with more processing and property-measurement experiments. Our goals were to reduce density and cell size, improve uniformity, develop techniques to measure uniformity, test foams for performance under target conditions, and improve foam processing reproducibility. We also started an investigation of a new foam material, cellulose acetate (CA), which is made by a phase separation technique.

In the first article of this report, "Polystyrene Foams," we discuss our continuing development of these materials. This year we concentrated our efforts on perfecting the formulation, determining the best polymerization conditions, investigating the drying process, assessing alternative homogenization techniques, and using statistically designed experiments to determine the reproducibility of foam preparation. PS foams can now be prepared with good uniformity at a density of 85 mg/cm³ and a cell size of 2 to 3 μm using our syringe-pump mixing apparatus. Foams with densities of 50 mg/cm³ and cell sizes of 3 to 10 μm can be made using a Brookfield counter-rotating mixer, but the uniformity is not as good.

We have also pursued the development of RF foams because they offer a much smaller cell size than PS foams, which should mean greater DT-fill stability. In last year's initial efforts, we obtained RF foams with a density of 150 mg/cm³ only with great difficulty. We can now consistently produce RF foams with a density of 20 mg/cm³. The reduction in the density is a result of our better understanding of gel formulation and processing.

We have recently taken on an additional avenue of research in the RF work. In an attempt to remove the small oxygen content of the foam and improve the mechanical properties, we have investigated carbonization. When heated to 1100°C in an inert atmosphere, RF foams lose hydrogen and oxygen to form a glassy (vitreous) carbon that is totally amorphous. Some shrinkage occurs during carbonization, but a foam density of 41 mg/cm³ has been reached. All of these developments are discussed in the article "Resorcinol-Formaldehyde Foams," later in this report.

In the article "Cellulose Acetate Foams" we discuss the investigation of this new foam material, which was first developed by R. W. Pekala. Our work has concentrated on studying the preparation and properties of the CA gel and on preparing CA foams by supercritical extraction. We have made foams with densities of 30 to 150 mg/cm³ with an estimated cell size of 0.1 to 1 μm. The reproducibility of foam preparation with respect to density is very good.

In the final article in this report, "Target-Related Foam Properties," we discuss target specifications and foam properties related to target production. We have measured foam density and density uniformity, wetting properties, hydrogen capillary pressure, machining properties, thermal contraction, and bonding properties. We have investigated molding of foams as a technique for producing materials more rapidly than by machining. We assess the advantages and disadvantages of each foam as a potential target material.

The quality of foam materials has greatly improved during this last year, and we now have three foam materials that have the potential to meet target specifications. We reduced density and improved density uniformity. We improved characterization of foams through new scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques, thermal analysis from room temperature to 15 K, and viscosity measurements of gels and emulsions. We assessed the feasibility of producing hemishells by diamond turning and grinding. We developed molding techniques for all three foam materials. In the future, our efforts will focus on improving foam preparation, measuring foam properties, comparing the foam materials, and developing target assembly techniques.

Polystyrene Foams

Introduction

We are continuing to develop PS foams using an inverse-emulsion system originally developed by Unilever Research Laboratory.³ A water-in-oil, high-internal-phase emulsion is made by using a surfactant such as sorbitan monooleate (Span 80) and a water-in-oil ratio of 90/10 to 95/5. The oil phase is a 50:50 mixture of styrene and divinylbenzene (DVB) monomers, and the surfactant is

usually 20 wt% of the oil phase. The DVB is added to increase the strength of the foam through crosslinking. The water phase contains sodium persulfate as a polymerization initiator. After polymerization, the resulting foam is dried in a vacuum oven to yield a material with a density of 50 to 100 mg/cm³. The structure of the foams and the details of the process for making them are described in Ref. 4. Previous development work is described in Ref. 5.

We have continued our studies of the chemistry of this system by assessing alternative surfactants and initiators. We have examined what effect adding aluminum

chloride has on foam structure. We have investigated the relationships between PS molecular weight and initiator concentration and temperature, and the effects of polymerization accelerators.

The polymerization has been followed using both optical microscopy and viscometry. We have carried out several studies of the foam drying process, and we have investigated methods for removing the surfactant and initiator from the foam.

Processing methods continue to be a focus of investigation. We have assessed the use of a peristaltic pump for mixing, and we have constructed and tested a new syringe-pump apparatus.

A statistically designed response surface methodology experiment provided us with an assessment of key variables and of the reproducibility of the foam-making process. The results led to a continuing study of reproducibility, which has as its goal the production of large numbers of samples for tests that will assess potential success as a target material. The results of these tests are described in "Target-Related Foam Properties" at the end of this report.

Emulsion Chemistry

We continue to use Span 80 as our surfactant since it has proven superior to the others we have tested. We briefly investigated the use of block copolymer surfactants, which were supplied to us by D. J. Meier of the Michigan Molecular Institute. These were compounds composed of blocks of polystyrene and polyethylene oxide. We thought they might be effective at stabilizing the emulsion and reducing the cell size because of the similarity of their lipophilic components to styrene. However, emulsions were not formed, and the systems separated into two phases. It is possible that this occurred because the amount of polyethylene oxide was too large, making the surfactants too hydrophilic. Since Span 80 gives satisfactory results, we have chosen not to pursue this approach further.

Although sodium persulfate acts effectively as a polymerization initiator in this system, it would be desirable to replace

it with a material of lower atomic number. We tested a variety of organic polymerization initiators, and we also tried some polymerizable surfactants, but these initiators and surfactants produced foams of low mechanical strength that have large cells with nodular walls. It seems likely that it is necessary to have a water-soluble rather than an oil-soluble initiator to ensure that the polymerization occurs at the interface rather than within the oil phase. We will continue to use sodium persulfate and will investigate the possibility of removing it from the foam after polymerization and drying if necessary.

We have also continued our investigation of the addition of aluminum chloride to reduce emulsion cell size. When an Osterizer blender was used, the addition of an optimum concentration of 0.01 wt% AlCl_3 caused a reduction in the cell size of the resulting foam to 2–3 μm , compared to a control sample with a cell size of 3–7 μm . However, when we tried this experiment with the syringe pump as the mixing device—which produces a foam with a cell size of 2–3 μm without AlCl_3 —no further reduction was observed. It is likely that geometric constraints prevent any reduction beyond the 2–3 μm limit.⁶ We will investigate the effect of AlCl_3 addition on foams made in Brookfield counterrotating mixers to see if the effect observed in the blender occurs with this mixing device, which also produces larger cells. We have preliminary indications that the addition of AlCl_3 may improve the uniformity of foams made at the lower end of our density range.

In *Laser Program Annual Report 86*⁷ we described an experiment designed to study the effect of polymerization temperature and initiator concentration on various foam properties. Four initiator concentrations (3.0, 6.2, 11.9, and 17.6 g/l) and three polymerization temperatures (40, 50, and 70°C) were used. (The initiator concentrations were incorrectly given in the 1986 article.) These foams were made without any DVB so that the molecular weights could be determined using gel permeation chromatography. Molecular weights are important because they may be correlated with foam strength.

Table 1. Analysis of PS polymerization as a function of temperature and amount of initiator.

Temperature (°C)	Initiator (g)	Surfactant (g)	M_n^a	Exp. ^b DP	Calc. ^c MDP	Active initiator ^d (%)	Active initiator (g)	Increase ^e (%)
40	0.60	15.0	144 730	1390	57	4.5	0.025	—
40	1.22	15.0	96 811	930	28	3.0	0.037	48
40	2.40	15.0	74 810	718	14	1.9	0.046	84
40	3.61	15.0	61 500	591	9.5	1.6	0.058	132
50	0.60	15.0	83 600	803	57	7.1	0.043	—
50	1.22	15.0	61 100	587	28	4.8	0.059	37
50	2.40	15.0	38 100	366	14	3.8	0.091	111
50	3.61	15.0	32 000	307	9.5	3.1	0.112	160
70	0.60	15.0	30 500	293	57	19.4	0.116	—
70	1.22	15.0	22 465	216	28	13.0	0.159	37
70	2.40	15.0	18 150	174	14	8.0	0.192	65
70	3.61	15.0	15 500	149	9.5	6.4	0.231	99

^a Number average molecular weight.^b Experimental degree of polymerization = $M_n/104$.^c Calculated minimum degree of polymerization = moles styrene/moles initiator.^d Percent active initiator = (Calc. DP)/(Exp. DP).^e Percent increase in active grams of initiator, based on grams used from the 0.60-g run at that temperature.

The results are shown in Table 1. The molecular weights decrease with increasing amount of initiator and with increasing temperature. It is clear that the amount of active initiator increases with increasing temperature. This is most probably because the initiator breaks down into radicals faster at higher temperatures. At a given temperature, the percent of initiator that is active decreases with increasing concentration. This may be related to the fact that the initiator is in the aqueous phase, and there are a limited number of interfacial sites where it can initiate.

The mechanism of a free-radical polymerization consists of four steps, which are shown below:

The first step is the dissociation step, where the initiator dissociates into radicals. This is followed by an initiation step, in which the radical reacts with the monomer, and then by a series of propagation steps in which the polymer chain grows through propagation of the radical species. The chain growth will terminate

if two chain ends find each other. The standard steady-state treatment of this mechanism leads to the following mathematical relationship between the degree of polymerization and the initiator concentration:

$$\bar{X}_n = \frac{k_p}{(k_t k_d)^{1/2}} \times \frac{[M]}{[I]^{1/2}} \quad (1)$$

The degree of polymerization should be proportional to $[I]^{-1/2}$. Figure 1 shows that this relationship is followed by the data from this experiment. This evidence is consistent with the free-radical mechanism. (It is likely that other forms of termination are also possible, given the large number of reactive species present, but they must be consistent with these results.)

We have assumed that it is desirable to polymerize the oil phase of the emulsion as fast as possible to minimize emulsion coalescence, which increases the cell size. The polymerization rate can be increased by raising the population of free radicals. This may be accomplished in three ways:

1. Increasing the concentration of initiator (the effects of which have just been described).
2. Increasing the temperature (which also increases the rate of coalescence).
3. Using an accelerator that increases the rate of dissociation of the initiator.

We have tried two accelerators: ferrous sulfate and N,N,N',N' -tetramethylethylenediamine. Several concentrations of both accelerators were tried at a series of temperatures. The emulsions were homogenized in a peristaltic pump. As with the previous experiment, no DVB was added because we wanted to be able to measure the molecular weights of the foams to assess the effect of the accelerator. The molecular weights of the foams were all in the range of 20 000 g/mol, regardless of the temperature or accelerator concentration. We now believe that the accelerator concentration was too high, and that polymerization occurred too rapidly, resulting in low molecular weights. The emulsions became extremely viscous during homogenization, and we believe this is because the oil phase was partially polymerized. Since more recent experiments indicate that the effect of coalescence at 50°C may be minimal, this approach will not be pursued further until the extent of coalescence is clearly established.

Polymerization Studies

In order to improve our understanding of the polymerization process, we prepared an emulsion using the Brookfield

counterrotating mixer and removed samples at 20-min intervals after placing the emulsion in a water bath at 50°C. The oil phase of the polystyrene emulsion consisted of 40 wt% styrene, 40 wt% DVB, and 20 wt% sorbitan monooleate. The calculated density was 50 mg/cm³. We examined these samples under an optical microscope. Figure 2 shows the emulsion before it was placed in the water bath and the sample that was removed after 1 h 40 min, which was the time when solidification was first observed. Areas of solid polymer appear to be forming, but the emulsion shows no substantial signs of coalescence. We took samples up to 3 h 20 min, at which time the system had become too solid to sample, and we observed no substantial coalescence through this time.

Fig. 1. Relationship between degree of polymerization and initiator concentration for PS foams.

(a) Zero time

(b) 1 h 40 min

Fig. 2. Optical micrographs of polymerizing PS emulsion: (a) zero time; (b) after 1 h 40 min at 50°C.

In order to confirm these results and to determine the rate of polymerization when no initiator is present, we repeated this experiment, replacing the initiator with an amount of sodium sulfate that would give the same ionic strength. In this case, it was 4 days before the emulsion began to polymerize, showing that the rate of purely thermal polymerization is negligible. Once again, we observed no substantial coalescence even over this much longer time.

It may be that the relatively large cells of emulsions prepared with the Brookfield mixer makes them resistant to coalescence, or that the surfactant forms a liquid crystalline phase at the interface that has a very high surface viscosity that stabilizes the emulsion. In order to resolve this question, we need to confirm the results using emulsions made with the syringe-pump apparatus. It is also possible that the microscope slide-making process may affect the results, although the consistency of structures seen throughout the two experiments leads us to believe that this is not the case.

We have also used viscometry to determine the time to polymerization of PS emulsions at various temperatures. Viscosity measurements lend themselves nicely to this, because during polymerization the system changes from an emulsion with a mayonnaise-like consistency to a solid. We selected a viscometer that vibrates a glass rod at 600 s^{-1} with a vibration amplitude of $25\text{ }\mu\text{m}$ in air. When this vibrating tip is inserted in a liquid, the viscosity can be determined by the amount of damping measured by a transducer at the top of the rod.

The emulsion formula, calculated density, and mixing method were the same as for the optical microscopy experiment. We poured the emulsion into the heated reaction flask and tamped it down to eliminate voids. We immersed the glass rod of the viscometer to a mark on the rod 1-in. up from the end. We made a cover from aluminum foil to limit the escape of heat and moisture from the cell. To maintain a constant temperature, we set up a temperature control bath to pump a water/ethylene glycol solution

Fig. 3. Logarithm of normalized viscosity of polymerizing PS emulsions.

through a jacketed reaction flask. As the emulsion polymerized, a logging multi-meter printed the data points generated by the viscometer. Most runs were for 24 h, with typical recording intervals of 3 to 10 min. The raw data consisted of an uncorrected viscosity measurement, the temperature of the emulsion, the date, and the time.

The viscometer output is the product of viscosity and the sample density. Since the emulsion has a density of approximately 1 g/cm^3 , we read the data directly as viscosities in centipoise. In analyzing the data, we divided all the viscosities by the initial viscosity to eliminate some of the scatter. Since the viscosity changed by several orders of magnitude during a run, we took the logarithm of the normalized viscosity (η/η_0). When the data for all of the runs are plotted versus time (Fig. 3), the results show a trend of decreasing time to polymerization with increasing temperature. The greatest increase occurs between 30 and 40°C. Note that the inflection in each curve represents roughly a factor of 30 increase in viscosity.

To verify that the transition did signify polymerization, we made an emulsion with ethylbenzene in place of the styrene/DVB mixture. After 24 h at 50°C, no transition had occurred, and the viscosity decreased slowly with time. Each of the runs was duplicated at least twice with generally the same results. The reproducibility of the time to polymerization at 50°C among three runs was within one hour. As polymerization progresses, the viscosity increases until the material no longer behaves like a liquid, and the viscometer can no longer make useful measurements. Thus, it is not possible to determine the total time period of polymerization with this method. It is clear, however, that the time to onset of polymerization at 50°C agrees well with the time determined in the optical microscopy experiment.

Drying Studies

Once a PS emulsion has polymerized, the water must be removed from the foam structure by drying in a vacuum oven to produce the void space within

the foam. To shorten production time, it is desirable to remove the water as rapidly as possible without damaging the foam. The drying rate may also reveal something about the structure of the foam.

We have found that the water will rust out the mechanical vacuum pumps normally used on the ovens. To solve this problem, we selected a new type of vacuum pump that works on a venturi principle because it would pass the water without any harmful effects. The mechanical pumps would evacuate an empty chamber to a base pressure of approximately 50 mTorr, but the base pressure for the new pump was approximately 7 Torr. We were concerned that the rate of drying would decrease, thus slowing the production rate of PS foams, but initial comparisons between the two pumps yielded similar drying rates. This prompted a study to determine the mechanisms of the drying process and to see if its efficiency could be improved by changing the temperature and pressure.

In order to measure the rate of water removal with time, we placed an electronic balance with a remote display unit inside a vacuum oven. The remote display unit had an RS-232 output, which was fed to a computer for data logging. Logging intervals were typically 10 min.

The oil portion of the PS emulsions used for this experiment consisted of 42 wt% styrene, 42 wt% DVB, and 16 wt% sorbitan monooleate. We emulsified the samples using a counterrotating mixer; the densities were approximately 80 mg/cm^3 . We polymerized the emulsions in 50-ml plastic syringes in an oven at 50°C for 24 h. After polymerization, we sectioned the container with a band saw, leaving cylindrical sections that were 0.5- or 1.0-cm thick with the sides still enclosed in plastic. We placed the samples in the vacuum chamber on the zeroed balance, initiated data logging, and activated the vacuum pump.

Simply viewing the data as weight vs time produces a declining curve that yields little information on the mechanisms that drive the drying process, but one can determine the total amount of time it took to dry the sample. There is initially a sharp increase in the drying

Fig. 4. Drying rates vs moisture content for 1.0-cm thick PS foam samples.

Fig. 5. Drying rates vs moisture content for 3.0-cm thick PS foam samples. ▼

rate due to the evaporation of surface water. The rest of the drying process is relatively slow. Inconsistencies in producing the samples caused slight variations in length that do not affect the area through which evaporation occurs, but do increase the volume of water removed. Since this determines the amount of time to complete the drying process, and the purpose of the experiment was to compare the rates of drying, we normalized the volume of water by plotting the drying rate as a function of the ratio of the weight of water to that of dry foam. Since all of the samples were made to the same bulk density, and the ratio of water to foam is constant, the drying rates can be compared. Figure 4 shows the results of three runs plotted in this manner.

We made the first run with the oven at ambient temperature and the venturi pump achieving a base pressure of

Fig. 6. Sample temperature vs moisture content for 3.0-cm-thick PS foam samples: (a) room temperature; (b) at 50°C; (c) with nitrogen purge.

8 Torr. The second run was also at ambient temperature but with a mechanical pump, which achieved 200 mTorr. There is very little difference in the two rates, and the total drying time for both was approximately 8 d. The third run used the venturi pump but was made with the oven at 50°C. In this case, the rate of drying roughly doubled, and the samples dried in about 4 d.

The increase in drying rate with temperature is to be expected, because of the increase in the rate of evaporation of water, but the lack of any pressure effect was somewhat surprising. In order to get more information about the process, we attached a vacuum transducer to the oven so that pressure could also be logged with each weight reading. We measured and logged the internal temperature of the foam sample to determine the amount of temperature drop due to heat loss from vaporization.

The emulsion formula and method of preparation were the same as for the previous experiments, but we cast the emulsion in a 250-ml Nalgene container with 30-gauge type J thermocouples arranged so that the junction was in the middle and the leads exited separately through small holes drilled on opposite sides of the container. Each sample had three thermocouples that we spaced top to bottom so that one was in the center and the other two were 0.5-cm and 1.0-cm in from their respective surfaces. We performed polymerization as before, and sectioned the container into plastic-encapsulated cylinders roughly 3 cm long with two exposed faces 6 cm in diameter. We placed the samples in the vacuum

chamber on the zeroed balance, and placed a fourth thermocouple so that it touched the center of the surface of one end of the sample. We initiated data logging and activated the vacuum pump.

The results of three runs made with this system are shown in Fig. 5. The shape of the curves has changed somewhat with these larger samples. The effect of increasing temperature is again observed. The sample that dried out at room temperature took 8 d, and the one that dried at 50°C took 4 d. To test the effect of increasing the flow through the vacuum oven, we ran a sample in which a dry nitrogen gas feed was attached through a needle valve to the drying oven, raising the base pressure from 8 Torr to 11 Torr. This also increased the drying rate: one sample dried in 2.5 d and another in 4 d.

More information can be obtained when the sample core temperature is plotted vs moisture content, as in Fig. 6. In the beginning, the water-to-foam ratio is a little over 11:1 and the sample is still at a slightly elevated temperature. After the vacuum pump is turned on and the water begins to evaporate, temperature throughout the sample drops sharply because of the loss of heat of vaporization. The temperature remains depressed until nearly 80% of the water is removed, which occurs in only about half of the total drying time. At this point the temperature begins to rise from the outer regions of the sample towards the center.

In the case of the sample with the nitrogen purge, the internal temperatures dropped below 0°C, indicating that the water may have frozen. If this is the case,

it will be necessary to determine whether this has any deleterious effects on foam structure. In a preliminary experiment on another vacuum oven system, SEM analysis showed no changes, but this needs to be confirmed.

These temperature measurements and preliminary x-ray radiography experiments on partially dried foams suggest that the water surface is moving from the outside of the foam to the center. Our next step is to develop a model of the drying process that explains this.

Removal of Surfactant and Initiator

As a potential target material, the foam ideally should not contain any substances other than the polymerized styrene and DVB. Therefore, we have tried to remove the Span 80 and the sodium persulfate from the foams.

To remove the Span 80, we have tried two methods. In one, 30 wt% of the Span 80 was removed by heating a dry foam at 85°C in a conventional oven until a constant weight was reached. We have recently determined that the foam can probably survive heating to 115°C, so we will try increasing the temperature to remove more surfactant. In the second method, 90 wt% of the Span 80 was removed by immersing a dry foam in fresh hexane, which was exchanged daily for one week, and then by drying at 85°C. Hexane wetting and SEM tests indicated that the foam retained the same porous cell structure and wettability after treatment. In a second experiment with hexane removal, we used a Soxhlet extractor for 4 d with boiling hexane. However, only about 64 wt% of the Span 80 was removed, and there was some shrinkage of the sample, so that the reduction in density was not as great as expected. Radiography of this sample showed that the extraction was not uniform. We will do more work with both of these methods.

To remove sodium persulfate, we put dry foams in water for different periods of time, redried them, and then determined the concentrations of sodium and sulfur by elemental analysis. After 4 d in water, 99% of the sodium and sulfur was removed. (Although some sulfur should

be bound onto the polymer molecules as end groups, our results indicate that this involves very small amounts.) After 7 d, 617 ppm of sodium and 688 ppm of sulfur remained. Preliminary SEM analysis showed that the foams retained their porous cell structure, but that there was a distinct increase in surface roughness. It may be necessary to tolerate the presence of sodium persulfate unless another removal method can be found.

Processing Methods

Preparation of uniform emulsions with small cell sizes requires both the proper formulation and the proper homogenization techniques. The formulation determines the volume fractions of the emulsion phases and the interfacial characteristics. The homogenization apparatus provides both the necessary mechanical energy to break the coarse emulsion into fine droplets and the mixing to eliminate density variations. We have found that streamlined shear is best for our emulsions. Turbulence causes coalescence or inversion of the emulsion by disrupting the cell structure. Low shear produces an emulsion with a large cell size.

A second desirable feature of an homogenizer is the ability to produce material either continuously or in large batches. Our syringe pump is limited to 25-cm³ batches. Random mixing of the emulsion mixture in the syringe pump is not achieved because of the reciprocating nature of the syringe. For these reasons, we continue to look for improved mixing methods, even though the syringe pump currently gives us the best means of achieving target specifications.

Previously we reported on the use of a peristaltic pump to homogenize an emulsion.⁶ The early design, which consisted of a test tube with a side-arm inlet and a bottom exit, trapped air within the emulsion and did not provide random mixing. We improved both the equipment and the procedures for operating the pump this year. To assure uniform density, we first prepared a low-viscosity, large-cell emulsion using a low-shear homogenization technique. We poured the emulsion into a storage vat from which it

was fed by gravity into the peristaltic pump. The vat has a conical shape that is efficient for forcing all the emulsion to flow into the pump; it is made of polyethylene, which is not wetted by the emulsion, allowing the emulsion to flow to the exit. We then returned the output of the pump to the top of the vat where the emulsion flowed smoothly over the contents of the vat without entraining air.

We used this technique of mixing for preparing all the samples in the accelerator experiment. Unfortunately, mixing was hindered because the rates of polymerization were so high that the emulsion began polymerizing inside the pump. We need to assess this method using the standard formulation.

In addition to investigating the peristaltic pump, we also constructed a new syringe-pump device. We did this because the old pump was needed to begin experiments on molding PS and because we felt that several improvements could be made to the design. Figure 7(a) shows the apparatus with a load cell to measure the pressure on the syringes, and a thermocouple, which is taped to the outside of one of the syringes, to measure the temperature. This data is recorded on a strip chart recorder during a run. One syringe is filled with the water phase of the formula and the other with the oil phase. After all the air bubbles are removed, the syringes are connected with a plastic fitting and placed in the cradles of the pump. The fit is adjusted and the run started by turning on the air flow to the hydraulic pump. The pressure can be controlled, within limits, by regulating the air flow. A counting device on the carriage is connected to a control box so that the desired number of strokes can be carried out. Fig. 7(b) shows the two syringes in place before the start of a run. After just a few strokes, a creamy white emulsion is formed, as shown in Fig. 7(c). The new pump has been designated PUSH-ME-PULL-YOU-TOO (PMPY2). The original one, now dedicated to molding, is PMPY1. The concept for the syringe pump came from J. M. Williams at the Los Alamos National Laboratory.

Statistically Designed Experiments

In the *Laser Program Annual Report 86*,⁹ we described an experiment that was designed to optimize the formulation of the PS foam and to assess the reproducibility of foam preparation. This experiment was a three-variable, Box-Behnken response surface methodology (RSM)

Fig. 7. Syringe-pump mixing apparatus (PMPY2): (a) with load cell, thermocouple, and recorder; (b) syringes filled with oil and water before mixing; (c) syringes showing emulsion formation after mixing.

design with the concentrations of surfactant and initiator and the ratio of styrene to DVB as variables. After preparing the 15 samples in random order, as called for in the design, we looked at several emulsion and foam properties.

Several important decisions had to be made about the factors and their ranges and about certain parameters that had to be fixed. The units and ranges for the factors were chosen empirically as weight percents based on the way the foams are actually formulated. Although it is likely that molar concentrations and more strictly chemical factors may actually be controlling the system, our understanding of the basic chemistry is not sufficient to identify these.

The percents for each factor are on three different bases. For the percent styrene, the range is 0 to 100% of the monomer used, which means that we have foams that are made with 100% DVB, 100% styrene, and a 50:50 mixture. For the initiator, the percent is based on the amount of water phase, and the percent for the surfactant is based on the amount of oil phase. Hence, the percentages for the three factors do not sum to 100.

The size of the batch was fixed by the 25-cm³ capacity of the syringes, but in the case of density, a choice had to be made. We wanted to keep a constant target density of 50 mg/cm³, but, since the initiator and surfactant are not removed from the foams, the variation in these factors would have to be compensated for, particularly in the case of the surfactant, which constitutes as much as 35 wt% of the oil phase. This meant, however, that the amount of monomers had to vary in order to keep the total weight of the oil phase constant. In the case of the initiator, which amounts to a maximum of 1.5 wt% of the water phase, the decision was made to accept the relatively small variation in the density caused by not compensating for differences in the amount of initiator, because this compensation would have led to a variation in the ratio of water to oil phases. Since the surface properties of the interface are presumed to be very important in the behavior of this system, we judged this to be the greater risk.

We measured the emulsion droplet size by taking optical micrographs and measured the foam cell and pore sizes from scanning electron micrographs. We measured foam density and qualitatively assessed density uniformity through x-ray radiography. We attempted to measure BET surface areas, but the samples submitted turned out to be too small to give meaningful results, and there was not enough foam remaining to repeat the tests. We had also planned to measure the hexane wetting rate, as an indication of how hydrogen wetting would proceed, but discovered that the samples made with 100% styrene shrank substantially when put into the hexane; we have not found another solvent to replace it. Finally, we measured the compressive moduli of the foams. We analyzed the responses using the program X-STAT,¹⁰ which runs on an IBM PC computer. The model was the standard quadratic polynomial, and the coefficients were determined by a linear least-squares regression.

The most important information obtained from this experiment was that the structures of the three center-point foams, as determined by SEM, were widely different. One foam had the expected 2- to 3- μ m cells and was reasonably uniform; one had cells ranging up to 20 μ m; and the third had regions of apparent coalescence up to 1000 μ m across and was very nonuniform.

This was the first time that the reproducibility of the foam process had been checked in any systematic way, and the results indicated that it was very far from ideal. Our continuing efforts to investigate this problem are described in the following subsection on foam production. Unfortunately, lack of reproducibility meant that the statistics of the regression model were not particularly good, but we have drawn some qualitative conclusions that will need verification in future experiments.

Figure 8 shows that there appears to be a good correlation between the emulsion and foam cell sizes and the amount of surfactant used, as expected from the surface chemistry of the system and as indicated by earlier experiments. The

Fig. 8. Box-Behnken plot showing the effect of formulation on emulsion and foam cell sizes for PS foams.

Numbers in circles = emulsion cell size (μm)
 Numbers without circles = largest foam cell size (μm)
 *Range of 2–5 μm

other two factors do not seem to have a significant effect. There also appears to be a qualitative correlation between cell size and density uniformity. The statistics for the compressive modulus data were not really good enough to draw firm conclusions.

Foam Production

Our attempts to use the new syringe pump (PMPY2) were initially very frustrating. We were attempting to reproduce the formula that had been the center point of the RSM, and we consistently got foams with regions of coalescence or phase separation—as shown by the scanning electron micrographs—although the cell size was only 2–3 μm in the regions where this did not occur. When we raised the density to 85 mg/cm^3 , this problem immediately disappeared. At about the same time, we remeasured the density of the original 50- mg/cm^3 sample that had been the basis for the center point selection in the RSM. We discovered that the density of this foam had been incorrectly measured, and is in fact not 50 but 82 mg/cm^3 . Unfortunately, this result was incorrectly reported in the *Laser Program Annual Report 86*¹¹ and

was the basis for the conclusion that we could produce good 50- mg/cm^3 foams. [A scanning electron micrograph of this foam appears in Fig. 5-1(b) of that report.] Apparently, the amount of water needed for a 50- mg/cm^3 foam is too large to be stably incorporated into the emulsion, at least with the current formula. These results were confirmed by making several 50- mg/cm^3 foams using the old syringe pump (PMPY1). The same regions of coalescence were observed.

Another problem in producing consistently good-quality foams appeared when we looked at the x-ray radiographs of foams made with PMPY2, which showed concentric rings of high density. In this case, the problem was traced to differences between the two syringe pumps. We used the load cell to measure the pressure on the syringes in both pumps, and found it to be substantially higher in PMPY2. This is because improvements had been made in the design that reduced the drag of the carriage. We lowered the air pressure until the pressure on the syringes was the same in PMPY2 as it is in PMPY1, and the radiographs showed that the problem had almost disappeared.

Our next steps will be to attempt to optimize the operation of PMPY2 with respect to the pressure and the number of strokes, and to try to gain a better understanding of the mixing process. We will also be running experiments to lower the density and still maintain uniformity, either by increasing the amount of surfactant, which should stabilize the incorporation of more water into the emulsion, or by removing the surfactant after the foams are made.

Conclusion

During 1987 we substantially increased our understanding of the PS system, particularly in the area of reproducibility and in identifying key variables that control the system. We are now able to consistently produce good-quality 85-mg/cm³ foams with cell sizes of 2–3 μ m. We have promising leads for improving quality and lowering the density. We are able to supply foam materials suitable for many of the tests that need to be carried out for target properties, as described in the final article of this section.

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Resorcinol-Formaldehyde Foams

Introduction

The development of low-density foam materials from a resorcinol-formaldehyde system was initiated in 1986 by Pekala at LLNL.¹² Results obtained by his group are very similar to ours. Development work is described in the *Laser Program Annual Report 86*.¹³ The foams are promising as target materials because of their very small cell size, estimated at about 0.1 μ m, which offers potentially greater DT-fill stability than PS foams.

The synthesis of RF foams involves the condensation reaction of the monomers resorcinol and formaldehyde to form a sol-gel in a slightly basic aqueous solution at elevated temperatures, followed by supercritical extraction from liquid carbon dioxide to form a foam.

In the early stages of development, we could not control foam shrinkage, and foam densities were high and unpredictable. We have resolved these problems by improving the formulation and processing. We have also investigated carbonization of RF foams as a means of improving mechanical strength. We can now make foams with densities of 20 to 50 mg/cm³ that are promising in their quality and reproducibility as they apply to target design specifications.

We have employed additional techniques to characterize the foams in detail. To gain a basic understanding of the reaction kinetics of the gels, we have performed dynamic mechanical analysis studies. We are investigating transmission electron microscopy as a technique to resolve the very fine microstructures of the foams. We have also reduced the production time by a factor of 2. Molding of RF foams is discussed in the article "Target-Related Foam Properties" at the end of this report.

Foam Preparation

RF foam properties depend upon the degree of crosslinking and the morphology of the network structure. To identify key variables that may affect these two features, we performed a screening experiment,¹⁴ which showed that the factors that suppress foam shrinkage are low concentration of sodium carbonate initiator, high concentration of reactants, high molar ratio of formaldehyde to resorcinol (F:R), and long curing times. Results from another experiment show that a post-curing acid treatment also enhances crosslinking. We investigated the effects of formulation, curing temperature and duration, and different acid treatments on foam properties to further our understanding of the significance of each factor.

For the formulation studies, the first step was to conduct a three-variable Box-Behnken response surface methodology similar to the one performed for PS foams. We varied the reactant concentration from 4 to 8%, F:R from 1.6:1 to 2:1, and the concentration of Na_2CO_3 from 0.025 to 0.08 wt%. We prepared the foams in random order.

First we mixed and stirred the reactants at 70°C for 2 h. Then we cured them at 70°C for 7 d inside sealed ampules before washing them in 5% acetic acid at 50°C for 1 d. We then put the gels through a series of solvent exchange steps: they were placed in methanol, amyl acetate, and then liquid carbon dioxide for 7 d each. The CO_2 was taken above its critical temperature and was bled off slowly to avoid passing a liquid meniscus through the material.

The densities of these foams are shown in Fig. 9. It is apparent that Na_2CO_3 plays a dominant role in controlling foam shrinkage. For a fixed amount of reactants, all foams having the lowest densities were obtained from formulations with the lowest concentration of Na_2CO_3 . The effect of F:R appears less significant. The lowest density obtained from this study was 57 mg/cm^3 , but this foam fractured easily when being cut or touched.

In the curing study, we fixed the formulation at 6 wt% reactants, F:R at 2:1, and Na_2CO_3 at 0.05 wt%. We cured the mixtures at 70, 90, and 110°C for 7 to 14 d. We found that foam density is affected only by the curing temperature. The densities were in the range of 90 mg/cm^3 after curing at 70°C, and 80 mg/cm^3 after curing at 90 and 110°C. The compressive modulus of the foam, on the other hand, is affected by both curing temperature and time. We measured the moduli in the elastic region and found values between 1 and 2 MPa for foams cured at 70 and 90°C. Foams cured at 110°C had many cracks, and the moduli decrease as the curing time increases. All moduli were measured by compressing $1 \times 1 \times 1$ -cm cubes to a maximum of 10% strain at 0.1 mm/min. Since we were more concerned about lowering the density—as long as the foam had enough

Fig. 9. Box-Behnken plot showing the effect of formulation on foam density in RF foams.

structural integrity to sustain machining and tritium radiation at cryogenic temperatures—we selected 90°C and 9 d as the optimum curing conditions. To verify these results, we cured the formulation with the lowest density from the formulation study (57 mg/cm^3) at 90°C for 9 d. The resulting density was lowered to 48 mg/cm^3 , and the foam was not as fragile as before: it could be vibratomed into blocks with smooth surfaces.

The purpose of an acid treatment in RF foam processing is to assist in further condensation of hydroxymethyl groups remaining in the gels to form ether bridges between resorcinol molecules. We tried to enhance this effect by using stronger acids. One advantage of using a stronger acid is that a lower concentration achieves the desired pH, and this can prevent side reactions. We investigated 0.125-wt% trifluoroacetic acid and acetic anhydride. Their pH values at room temperature were 1.9 and 1.05, respectively, as against 2.19 for 5-wt% acetic acid. After they sat in the acids for 3 d at 50°C, we compressed the gels to a 5% maximum strain at 0.1 mm/min in an attempt to determine the extent of cross-linking by comparing their compressive moduli with those of the gels that had not been treated with acid. We found that the modulus increased by 50% after treatment with acetic anhydride, 75% after treatment with acetic acid, and 170%

after treatment with trifluoroacetic acid. However, we did not observe any significant improvement in foam modulus or foam density. Therefore, we chose to keep 5% acetic acid at 50°C for 1 d as our standard acid treatment since it is much less hazardous.

Key findings from these studies have enabled us to produce foams of very low density. By lowering the Na_2CO_3 concentration to 0.0125 wt% and using the optimum curing conditions and an acetic acid treatment, we can reduce foam shrinkage to less than 25%, and can consistently produce foams with densities in the range of 20 to 50 mg/cm^3 . All of these foams appear uniform in x-ray radiographs. While their low densities are attractive in that they would allow a lower target ignition temperature, these foams sometimes fracture during measurements of their thermal contraction. Details are given in "Target-Related Foam Properties" at the end of this report.

Thinking that the foams might contain internal stress because of crosslinking and/or vibratoming, we tried to eliminate this problem by annealing the foams, but without success. But an alternative technique that greatly improves the mechanical strength of RF foams is carbonization.

Carbonization of RF Foams

Carbonization is a process in which polymers are heated in an inert atmosphere to temperatures above 300°C. Reactions take place initially within the C-C chain: Depending on the chemical structure, the chains can either degrade into small molecules, collapse to form aromatic lamellae, or remain intact and coalesce with neighbors.

We have been using the carbonization facility in the Chemistry and Materials Science Department to carbonize RF. The procedure involves heating the foams in argon from room temperature to 1050°C in 12 h, maintaining 1050°C for 4 h, and then cooling down to room temperature in 1 d. RF generally retains its shape, but its shrinkage is greater than its weight loss, which results in an increase in density. This leads us to believe that the mechanism of RF carbonization is similar to that of many other organic materials: at temperatures below 300°C, RF turns black and loses excess monomers and solvents. Between 300 and 500°C, it undergoes a rapid weight loss in which oxygen and nitrogen are removed, and beyond 500°C, hydrogen is gradually eliminated. The C-C chains then coalesce to form a large network of aromatic rings. Elemental analysis reveals that an RF foam contains 62 wt% carbon and 38 wt% oxygen, nitrogen, and hydrogen, whereas its carbonized counterpart (CRF) contains 93 wt% carbon and 7 wt% oxygen, nitrogen, and hydrogen. We do not yet know what the source of nitrogen is in the foams.

The most striking result of carbonization is a tremendous increase in compressive modulus. An early study showed that an RF foam with a density of 48 mg/cm^3 has a modulus of 0.1 MPa, whereas its CRF foam has a density of 77 mg/cm^3 and a modulus of 8.7 MPa. To bring the density of the CRF foams to less than 50 mg/cm^3 , we carbonized RF foams with densities less than 40 mg/cm^3 .

We discovered that the increase in density as a result of carbonization depends on the Na_2CO_3 concentration and on the foam density before carbonization. Generally, foam density increases by 50% after carbonization. If the Na_2CO_3 concentration is high, or the foam density before carbonization is in the range of 20 mg/cm^3 , the density increases by more than 100% after carbonization. At present, we can produce CRF foams with densities less than 40 mg/cm^3 . Like RF foams, CRF shows a uniform density distribution in x-ray radiographs (Fig. 10). Other target-related properties appear

Fig. 10. X-ray radiographs of cylindrical samples of (a) RF foam, (b) CRF foam. The dents are surface defects caused by mishandling.

promising and are discussed in the final article in this section.

Other Formulations

We have investigated other resorcinol-based materials to see if we can achieve a network with increased and more uniform crosslinking. To increase crosslinking, we substituted catechol (1,2 dihydroxybenzene) and hydroquinone (1,4 dihydroxybenzene) for resorcinol (1,3 dihydroxybenzene). Since each of these isomers has four potentially active sites compared to the three possessed by resorcinol, tetra-functional crosslinking may occur. However, an analysis of their electronic resonance structures shows that, unlike resorcinol, in which all three sites are potentially active, in these isomers only two sites have significant activity, and the other two are less active. The reaction in tetra-functional systems would, at best, be slow.

Although we made a gel with catechol, the foam obtained had a density of 440 mg/cm^3 ; a longer reaction time might have yielded better results. In the case of hydroquinone, a gel was never formed; we obtained only a precipitate, regardless of pH.

To increase uniformity, we tried phloroglucinol (1,3,5 hydroxybenzene) because it has three equally active sites. Preliminary studies showed that low concentrations of Na_2CO_3 , high F:P molar ratios, and low curing temperatures contributed to lower-density foams.

We also set up a two-stage reaction with phenol-resorcinol-formaldehyde. The object was to first make linear prepolymers of phenol with formaldehyde by using an ortho-directing catalyst and then react these prepolymers with resorcinol and formaldehyde to make a crosslinked network. Such a procedure has the possibility of controlling network structure. We produced a crumbly, pink foam with a density of 55 mg/cm^3 using triethanolamine as the catalyst.

Of all the alternatives we have looked at, phloroglucinol is the most promising candidate. We may resume our research effort in this area, depending

on the outcome of RF and CRF foam development.

Dynamic Mechanical Analysis of RF Gels

To increase our basic understanding of the RF system, we used several methods of mechanical testing to follow the changes in the visco-elastic properties of RF gels as they undergo condensation polymerization. The goal of this study was to characterize the rheological properties of the gel to determine whether it would yield a good foam at the early stages of gelation. This would allow a reduction of 2 to 4 wk in the processing time.

We used a mechanical testing machine to measure the change in compressive modulus with polymerization (cure) time. For this experiment, a formulation of 2:1 F:R, 6 wt% reactants, and 0.05 wt% Na_2CO_3 was used. A batch of this mixture was sealed into 40 ampules and put in an oven at 70°C . Data was taken over a 40-d period by removing three ampules from the oven at various intervals and compressively testing the gels.

Figure 11 shows the results. The modulus reached a plateau after 20 d, and then continued to rise slowly. Extrapolating to infinite time, the maximum compressive modulus was calculated to be $0.0594 (\pm 2\%) \text{ MPa}$. To reach, for example, 70, 80, and 90% completion, we calculate that the gels would have to be cured for 9.4, 15.0, and 31.7 d, respectively. In our current processing, gels are

Fig. 11. Compressive modulus of RF foams vs cure time.

cured for 5–9 d, which should produce gels that have only 70% of their maximum modulus. Although the acid treatment improves foam strength, the mechanical testing results imply that a considerably longer cure time may produce gels with even higher moduli, and this needs to be confirmed.

Dynamic mechanical spectroscopy was the second technique we used to follow the polymerization of the RF system. In this experiment we used a rheometer equipped with a Couette (concentric cylinder) viscometer. The outer cylinder is sinusoidally oscillated at a constant frequency and amplitude while the magnitude and phase angle of the force transmitted to the inner cylinder is recorded as a function of the time as the polymerization reaction proceeds.

We determined the shear storage modulus, shear loss modulus, and viscosity as the gel polymerized. We used the same RF formulation as in the compressive testing experiment, but we changed the temperature in different runs. We prevented water evaporation from the cell by placing a layer of mineral oil on the surface of the RF solution.

Figure 12 shows the shear storage modulus G' as a function of time for four RF gels polymerizing at temperatures ranging from 59.2 to 81.7°C. Increased temperature accelerated the rate of polymerization, as evidenced by the earlier increase in modulus at higher temperatures. At long times the modulus of the gels approached a limiting value independent of cure temperature, indicating that the degree of crosslinking is the same for all cure temperatures.

Fig. 12. Shear storage modulus of RF gels vs time and temperature.

As discussed above, the strength of RF gels was shown to be a function of the formulation. To quantitatively compare gels prepared with different initiator concentrations or at different temperatures, we needed to define a point in each run that is specific to that run and that is easily recognizable.

We have defined the gel point as the time at which G' vs time has the maximum slope. Using the gel-point data, we compared the reaction rates of gels that have initiator concentrations of 0.025, 0.05, and 0.1 wt%. We found that reducing the concentration by a factor of 2 slowed the rate by 57%, while doubling the concentration doubled the reaction rate.

Using compressive and dynamic mechanical testing, we followed the polymerization of RF gels. The rate of reaction was found to be directly proportional to the initiator concentration. We found that increased temperature accelerates the reaction as expected but does not produce a stronger gel. We plan to use this dynamic mechanical technique to study the effects of other formulation variables on gel properties and reaction rate.

TEM Analysis of Foam Structure

Transmission electron microscopy (TEM) has been used on RF and CRF foams in an effort to identify their basic structures. By using a scanning electron microscope equipped with a field-emission gun at low voltage, we were able to tell that RF has a fibrous structure with a cell size of less than 0.1 μm . However, we were never able to resolve the structure fully; preliminary TEM results revealed that both RF and CRF are actually composed of interconnected beads, as in the case of silica aerogel. The bead size is on the order of 100 Å, with a pore size roughly five to ten times larger. BET surface area analysis reveals that RF foams have surface areas of 555 m^2/g , and CRF foams have surface areas of 705 m^2/g .

Production Time Reduction

The standard procedures for making RF foams are long and tedious. It takes 31 d to obtain a foam with a 1.5-cm

diameter (from a 10-ml ampule): 9 d for curing, 1 d for acid treatment, and 21 d for solvent exchange and drying, and the 10-ml size is only good for preliminary tests. When we get to the target-making stage, we would prefer a thicker sample, first because the foam might have inhomogeneities in the outer region, second because the foam might shrink to less than the target diameter after carbonization, and third because we could allow more room for machining. A foam with a 2.5-cm diameter (from a 50-ml ampule) would be satisfactory, but it would require a longer period for acid treatment and solvent exchanges.

To make production more efficient, we have attempted to minimize the time in the solvent exchange steps for both sizes of foam. We have tried direct supercritical extraction of water, and have tried exchanging water with methanol, isopropyl alcohol, or acetone before exchanging with liquid CO₂. We also tried direct extraction from isopropyl alcohol after the exchange with water. Only isopropyl alcohol and acetone followed by CO₂ were found to give good foams. To accelerate diffusion, we have increased the temperature from room temperature to 45°C in the first step, and have flushed the supercritical extractor more frequently during the exchange with liquid CO₂. Preliminary studies show that a gel with a 1.5-cm diameter takes 3 d in the first solvent exchange and 3 d in liquid CO₂, whereas a gel with a 2.5-cm diameter takes 5 d in each. This means we have reduced the production time of the smaller foam to 16 d from 31 d, and that of the bigger foam to 20 d from more than 31 d.

Conclusion

The development of RF foams progressed rapidly in 1987. We have investigated the effect of formulation and process variables on foam properties, and have reduced production time. We are now able to produce foams with densities as low as 20 mg/cm³ in 16 d. We are utilizing carbonization to improve the mechanical strength of the foams; the lowest density CRF foam has a density of less than 40 mg/cm³. Both the RF and

CRF foams appear to have uniform density distributions and cell sizes of less than 0.1 μ m. We are now examining their behavior with respect to target specifications, as described in the final article of this section. Based on the information we have collected, we think RF and CRF foams are very promising materials for direct-drive ICF targets.

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Cellulose Acetate Foams

Introduction

Cellulose acetate foams hold promise for direct-drive ICF targets because of their extremely small cell size, which appears to be in the range of 0.1 to 1 μ m. Current SEM techniques make it difficult to verify this cell size since it is below their resolution, but we plan TEM work similar to that done for RF foams.

The idea for developing CA foams as low-density materials originated with R. W. Pekala, who based the idea on the thin membrane technology of CA and on some work indicating that benzyl alcohol would be a very effective solvent for this process.^{15,16} We began our development of CA foams this year, and are making good quality foams with densities of 40 to 50 mg/cm³ and cell sizes less than 1 μ m.

The structure of the foam is determined by a phase separation technique similar to the one used to make polyethylene foams.¹⁷ The foams are machinable, appear to be moldable, and wick liquid hydrogen. We have conducted gelling studies to correlate the cooling rate and gel composition to the structure and strength of the dried foams. We have studied CA foams from gel concentrations of 2 to 15 wt%. The compressive moduli of the foams range from 0.3 to 28 MPa for 3 to 15 wt% gels, respectively.

Fig. 13. Scanning electron micrograph of CA foam.

Fig. 14. X-ray radiograph of CA foam.

The densities of the foams are predictable as a function of gel concentration.

Gel Preparation

The foams are made by a phase separation technique based on the solubility behavior of CA in benzyl alcohol. At temperatures greater than 45 to 50°C, CA has a very high solubility, but below 45°C the solubility drops sharply. The cooling is done in a water bath at programmed rates of 20 to 35°C per hour. This allows the foams to be made in the following manner: The CA is dissolved in benzyl alcohol at 110°C and then cooled to 30 to 45°C, at which point gelation takes place. A series of solvent exchanges from benzyl alcohol to carbon dioxide is required to allow supercritical drying from carbon dioxide. First, benzyl alcohol is exchanged for toluene, then the toluene is exchanged for liquid carbon dioxide, and finally the carbon dioxide is supercritically

extracted. The entire process takes 5 to 7 d.

Foam Properties

The densities of the CA foam materials, which can be cast in very large bricks, range from 28 to 225 mg/cm³, corresponding to gel concentrations of 2 to 15 wt%, respectively. The densities are higher than we calculated due to some shrinkage resulting from the drying process. A scanning electron micrograph of the foam structure is shown in Fig. 13. As with the RF foams, it is very difficult to extract reliable structural information because the resolution is poor. An accurate assessment of foam structure will be made from a TEM study similar to the one done for RF foams. The x-ray radiograph in Fig. 14 shows that the material is very uniform.

The compressive moduli of the foams range from 0.3 MPa for 3 wt% gels to 28 MPa for 15 wt% gels. BET surface area analysis yielded values of 600 to 800 m²/g, which is similar to the values for RF and silica aerogels. We have measured the thermal contraction of the foams from 300 to 20 K and determined it to be a 0.6% contraction in linear dimension. Additional foam properties are described in "Target-Related Foam Properties" at the end of this section.

Alternative Chemistries

We looked at other cellulose esters to see if the mechanical properties of the foams would be improved. These have the basic cellulose structure,

but have different types of esterification of the hydroxyls on the ring. The materials used were cellulose triacetate (CTA), where R, R', and R'' are acetate; cellulose acetate butyrate (CAB), where R is acetate, R' is butyrate, and R'' is hydrogen;

and cellulose propionate (CP), where R is propionate and R' and R'' are hydrogen. We prepared all of these using the same method, and they behaved similarly except for some differences in physical properties—mainly their solubility in benzyl alcohol. The CP dissolved in the benzyl alcohol, but did not separate out when cooled. The CTA and CAB dissolved, and phase separation occurred when they were cooled; these gels were processed and dried to foams. A 3.8-wt% gel of CTA yielded a foam with a density of 80 mg/cm³ and a compressive modulus of 0.56 MPa. The CTA foam was more rigid to the touch than CA foams due to its larger percent of crystallinity. CTA also requires a higher temperature to dissolve than the other cellulose esters and is more difficult to get into solution. The processing of the CAB gel was the same as for CA and CTA through the solvent exchange steps, but the CAB gels collapsed almost immediately when they were pressurized in the supercritical extractor with liquid carbon dioxide, making CAB unsuitable for foams made by this process. We do not have an explanation for this result.

We are also investigating a solvent/non-solvent system for producing a CA gel. In this process the CA is dissolved in a solvent and the solution is placed in a permeable membrane container in which the solvent is exchanged with a nonsolvent. The solvent and nonsolvent we used were acetone and methanol, respectively. A gel is formed by precipitation as the solvent is exchanged with the nonsolvent. The gel is then placed in methanol for a more thorough exchange of the acetone, and finally the methanol is exchanged with liquid carbon dioxide, which is supercritically extracted. We are still evaluating this approach.

Viscosity Measurements, Cooling Rate Effects, and Thermal Analysis

We undertook viscosity and cooling rate studies to determine the gelation points of the CA/benzyl alcohol solution and to find an optimum cooling rate to control foam morphology to improve mechanical strength. We made measurements of viscosity vs temperature as a function of time to determine the gel

Fig. 15. Viscosity vs temperature in CA gels for various concentrations.

Fig. 16. Densities of CA foams vs gel concentration.

Fig. 17. Compressive modulus vs density for CA foams.

point of the CA solution. We measured the viscosities with a vibrating rod viscometer. We prepared the gels in 3- to 15-wt% concentrations, placed them in a jacketed reaction vessel, and cooled them from 90 to 20°C during 3-, 10-, and 48-h periods. We controlled cooling rates by a refrigerated circulator bath and temperature programmer. We placed additional samples in the bath to be cooled at the same time as the viscosity sample so that the gel point could be observed visually.

Figure 15 shows that all the viscosities change at approximately the same rate but have different values. The gelation point is seen as a sharp increase in viscosity at temperatures ranging from 33 to 45°C, depending upon gel concentration. The gel point increases with increasing concentration as expected, and the rise in viscosity matches the observed gelation points of the solutions.

In Fig. 16, the densities of dried foams made from the gel samples are shown as a function of gel concentration. The densities are very reproducible and are essentially independent of the cooling rate. There is a linear correlation between density and gel concentration.

Figure 17 shows preliminary measurements of the compressive modulus. There is an increasing trend with increasing density as expected, but the cooling rate appears to have little effect. We submitted the 3-wt% foams for x-ray crystallography analysis, which indicated that all the samples were amorphous; there were no observable differences in the structures of the 3-wt% foams cooled at the different rates. We may have to use small-angle x-ray scattering to observe any crystalline junctions.

A comparison of differential scanning calorimetry results for the CA starting material and the dried foams showed no differences, which indicates that there is no chemical change in the CA during the foam-making process.

Conclusion

During our first year of making cellulose acetate foams we have produced a promising material for target foam. Next year we will concentrate on improving our formulation and processing methods and will make additional tests of foam properties.

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Target-Related Foam Properties

Introduction

We are conducting investigations of foam properties that are directly related to the target specifications described in the introduction to this section. We are developing techniques for quantifying density uniformity, for measuring wetting properties with both liquid hydrogen and liquid DT, and for measuring thermal contraction from 300 to 15 K. Radiation stability is assessed as part of the DT wetting experiments. We are evaluating various machining techniques, and tests are under way to identify an agent suitable for bonding hemishells together. Because machining is not an efficient method of producing large numbers of targets, we are also investigating molding of foams.

Density Uniformity

The specification for target density uniformity is somewhat ill-defined, but is generally given as uniformity of the projected or radial density to within 1% variation between areas 30 μm in diameter.

As described in the earlier articles in this section, we have used x-ray radiography to make a qualitative assessment of density uniformity and to locate defects such as voids and high-density particles. However, to verify that the foams meet target specifications, we need a quantitative technique.

Since the foams are opalescent and transmit light—although with considerable scattering—the question arose as to whether this light could be used as a quantitative method for determining foam density uniformity. We conducted two types of experiments: contact printing from a point source of illumination, and scanning densitometry with a photometer.

In the first experiment, we placed a piece of foam on top of a photographic plate, which we exposed by switching on a point source of light. We then developed the plate to reveal the light transmitted through the foam. Comparison of the transmitted-light photograph and an x-ray radiograph shows similar patterns within the nonuniform foam. To quantify the light transmission, we tried digitizing the photograph using a scanning microdensitometer, but this approach took much time and seemed to lack intensity resolution.

We took a more direct approach in the second experiment by using a stepper-motor-driven stage on a microscope equipped with a photometer. We scanned a piece of foam with a 25- μm void, and from measurements of the change in intensity, we calculated the void size to be 25 μm . After this first experiment, which was operated manually, we interfaced the equipment to a computer that controlled the stage motion and collected the photometric intensities. We analyzed the data and plotted them using the VIEW program on the LEAF computer system. Figure 18 shows an automated scan through a step wedge of foam. The step heights are 0.6, 0.8, 1.0, 1.2, and 1.5 mm. The intensity was sampled at 120 μm intervals. On the second step from the top, two small density increases are apparent as depressions in the intensity.

We are also developing a method of scanning an x-ray beam over the surface of the foam and measuring the

Fig. 18. Photometric scan of PS foam step wedge.

transmitted intensity. This is called point-by-point radiography. We have assembled the equipment and written the computer programs needed to analyze the data. We plan to begin testing on foam samples shortly.

In addition to our work on experimental measuring techniques, we have developed a well-defined computer model that closely resembles the features of PS foams. The objective here is to study the relationships among cell size, cell-size distribution, foam density, and radial density uniformity.

The model is constructed as follows: A box with dimensions of $40 \times 40 \times 20$ is set up and filled with spheres that represent the water droplets of the emulsion. In order to fill the box, we start by placing spheres of unit radius randomly in the box in such a way that they do not intersect; the dimensions of the box are defined in terms of the radius of these largest spheres. When all spheres of this size that will fit within the box have been inserted, the box is scanned and the interstitial locations are filled with the largest spheres that can be accommodated without having two spheres intersect. This placing of spheres is continued until the radius of the largest sphere that can be placed is smaller than some predetermined size, in this case 0.1. In order to avoid concern with the ordering effect of

flat surfaces, the box is constructed with periodic boundary conditions. This means that the bottom of the box is actually in the same plane as the top of the box, so that a sphere can be placed at a distance less than its radius from the bottom, and the part of the sphere that leaves the bottom of the box reenters at the top. The same conditions are applied to the sides. As long as the box dimensions are large compared with the sphere radii, this represents an efficient method for accurately modeling the interior of a piece of foam.

Since the spheres are meant to represent the cells in the foam, they are said to be empty, and the PS fills the interstitial spaces between the spheres. The density of the system is then

$$\rho = 1 - \frac{\sum_i \frac{4}{3} \pi r_i^3}{V_{\text{box}}}, \quad (2)$$

where the sum is over the spheres of radius r_i , and V_{box} is the volume of the box. Normally, the sum is taken from the largest to the smallest spheres; in this way, we can look at systems of different densities by truncating the sum when the desired density has been reached. (Here and throughout this discussion we are

assuming a polymer density of unity. Actual bulk densities can be inserted without difficulty.)

As expected, as the spheres get smaller, more can be fitted into the structure. In Fig. 19, we plot both smallest sphere radius and system density as a function of the number of spheres added.

As noted above, our primary interest is in the density uniformity projected through the sample. For our model the projected density is easily calculated as follows: In setting up the model, the stored information includes the coordinates a , b , and c of each sphere along with its radius r . Thus the equation of sphere i is

$$(x - a_i)^2 + (y - b_i)^2 + (z - c_i)^2 = r_i^2. \quad (3)$$

If we want to project the mass (the space between spheres) onto the (x,y) plane, and if in the box the z direction is represented by the box height of 20, it is easy to see that the projected mass m at the point (x,y) is given by

$$m(x,y) = 20 - 2 \sum_i [r_i^2 - (x - a_i)^2 - (y - b_i)^2]^{1/2}. \quad (4)$$

In Eq. (4) only those spheres that intersect the line parallel to the z -axis that passes through the point (x,y) are included in the sum. The projected density is simply $m(x,y)/20$. Thus, a grid of projected densities of arbitrary mesh size can be set up. In the work reported here, we used a mesh of 256×256 . One can easily take the projected densities at these points and calculate the average density in the square areas defined by the points by taking a simple average. In a similar fashion, average projected densities over larger square areas can also be computed, allowing an examination of fluctuations in density from area to area as a function of area size. In addition, we can look at the projected density as a function of slab thickness by simply projecting only some predetermined fraction of the distance through the sample.

Fig. 19. Model of PS foam density. Sphere radius and system density are plotted vs the number of spheres added.

To summarize, we have developed a model that allows us to look at projected density homogeneity as a function of sample density, sample thickness, and the size of the projected area. The results from this model follow.

Let us first examine the effect of overall density on homogeneity. In Fig. 20(a) we have plotted the frequency of deviation from the mean density against the percent difference from the mean density for projected areas of four grid squares (of size $40/256$ on a side in units of largest sphere radii) for systems with overall bulk densities of 0.2, 0.4, and 0.6. Note that as the density drops, the distribution becomes somewhat more narrow. The actual differences are more striking if we remember that the abscissa is in terms of percent difference from the mean. Thus 5% for the sample with a density of 0.6 represents an actual density deviation of 0.03, while the same percent deviation for the system with a density of 0.2 is only a deviation of 0.01. The more narrow distribution at lower density is, of course, a result of the broader distribution of spheres needed to lower the density to 0.2, which results in a more homogeneous distribution of the remaining mass.

The effect of sample thickness is shown in Fig. 20(b), where data for $\rho = 0.4$ is shown for both the full thickness of 20 and for the two halves of 10 each. The plot shows the expected result, namely a narrower distribution for the thicker sample resulting from the collective effects of randomly placing mass throughout the sample. The curves are roughly Gaussian, a fact easily checked

Fig. 20. PS foam density homogeneity effect of: (a) overall density; (b) sample thickness; (c) grid square size.

by noting that the ratio of their peak heights is roughly $\sqrt{2}$. This fact allows us to estimate the distribution for samples of arbitrary thickness. The Gaussian

nature of the model also manifests itself in Fig. 20(c), where the frequency of deviation is plotted for projected areas of 4, 16, and 64 grid squares.

We ultimately expect to acquire the foam homogeneity specifications in terms of the Fourier transform of the projected density as obtained from a radiograph. We will use our model to explore the nature of the transform for a system with a well-defined and adjustable structure. For example, we can easily create a system with a large defect and see how the Fourier transform changes with defect size. Work along these lines is in progress.

Foam Wetting Properties

Polymer foams used in laser fusion targets must be wetted with liquid DT. To help understand the dynamics of wetting and to characterize the foam, we use liquid hydrogen, which does not pose a radiation hazard. Hydrogen wetting measurements were made at the National Bureau of Standards using a cryogenic apparatus equipped with a balance. The foam samples were equilibrated at 20 K before starting the wetting experiment. To start the wetting, the foam was lowered until it just touched the liquid hydrogen. Foam weight was then recorded as a function of time.

Figure 21 shows the experimental liquid hydrogen wetting behavior of the foams we are investigating. Silica aerogel and polyethylene (PE) were also included for comparison.

The rate of wicking in increasing order is aerogel < PE < CRF < RF < CA < PS, which corresponds approximately with increasing pore size but may also depend on contact angle and foam morphology. For laser fusion targets a smaller pore size is desirable because it should provide a higher capillary pressure. This makes the target capable of sustaining a higher internal vapor pressure and allows it to tolerate variations in temperature without suffering a liquid blow-out. Thus, the materials having the lowest wicking heights are the most desirable from this standpoint.

We have already carried out a preliminary capillary pressure test on a PS foam sample. The value obtained was 0.75 psid

Fig. 21. Liquid hydrogen wetting behavior of low-density foams.

with hydrogen, which should correspond to ~ 1.5 psid with DT. Since this result is acceptable according to our calculations, we believe PS foam will work for our target design, although CA, RF, and CRF offer potentially improved target stability.

We are just beginning experiments to measure the rate of DT wetting in PS foams. The first step was to develop an annealing procedure that reduces the amount of residual water in the foam to a safe level, i.e., one that precludes formation of any hazardous amounts of T_2O . This has been accomplished: heating the foams to $115^\circ C$ for 24 h is sufficient. Another objective of these tests is to assess the radiation stability of the foam to the tritium. In one preliminary test, we exposed a piece of PS foam to DT for 72 h with no visually observable changes, but no quantitative data are yet available. Other foam materials will be tested after the PS work is completed.

In addition to our experimental measurements, we have continued our efforts to provide a mathematical model for wetting behavior. In the *Laser Program Annual Report 86*,¹⁸ we made use of the rate

of solvent wetting to estimate pore size in foam materials. Briefly, the rationale involves identifying the driving pressure P at any time as the difference between the pressure due to capillary rise and gravity:

$$P(t) = \frac{2\gamma \cos \theta}{r} - \rho h(t)g, \quad (5)$$

where γ is the surface tension, θ the contact angle, r the radius of the capillary, ρ the density of the fluid, $h(t)$ the fluid height as a function of time, and g the acceleration due to gravity. The rate of laminar fluid flow in a pipe is

$$\frac{dh}{dt} = \frac{r^2 P}{4\mu h}, \quad (6)$$

where μ is the fluid viscosity. We have a factor of 4 in the denominator rather than 8 as previously reported because in our application the rate of advance of the fluid height is twice the rate of advance of the center of mass of the fluid, which is actually what the equation should

address. Using Eq. (5) for P in Eq. (6) we get

$$\frac{dh}{dt} = \frac{r\gamma \cos \theta}{2\mu h} - \frac{r^2 \rho g}{4\mu} \quad (7)$$

If one is concerned only with the initial rate of rise, the second term can be dropped and the resulting expression integrated to give

$$h(t) = \sqrt{\frac{r\gamma \cos \theta}{\mu} t} \quad (8)$$

Thus a plot of $h(t)$ vs $\sqrt{t}$ allows the determination of r , if γ , μ , and θ are known.

This development is strictly valid only for laminar fluid rise in cylindrical capillaries, for which r is constant and well-defined. In our PS foam materials the structure more closely resembles 1- to 5- μm polyhedral cells randomly connected by small ($<2\text{-}\mu\text{m}$) pores. In

addition, issues of permeability and two-phase (fluid and air) flow in the experimental situation, long recognized as important by oil engineers, are ignored in the simple capillary model. Because of these problems, the approach would probably not have been pursued, except that the wetting data in fact show an excellent and reproducible $\sqrt{t}$ behavior. However, even if we accept the equations as they stand, we must still address the question of proper interpretation of capillary radius r from Eq. (8). In order to probe this issue, we solved a similar set of equations for a model, shown in Fig. 22, that includes both cells and pores. The cells are diamond-shaped with truncated height and diagonal length d , and they are connected at their corners with pores of diameter p .

As in the capillary problem, we will assume Eqs. (5) and (6) and start with the truncated Eq. (7),

$$\frac{dh}{dt} = \frac{r\gamma \cos \theta}{2c\mu h} \quad (9)$$

where we have replaced the h in the denominator of Eq. (7) with the actual side length subject to drag, ch , where c is a geometric factor that approaches $\sqrt{2}$ as p/d approaches zero. Also, r is now a function of the fluid level in the cell and this depends upon h , as well as upon d and p . We note again before proceeding that Eq. (6) is strictly valid only for flow in cylindrical pipes, a condition violated by the present model.

Integration of Eq. (9) leads to the result

$$h = \sqrt{\frac{\gamma(d - p \cos \theta)}{2c\mu \ln(d/p)} t} \quad (10)$$

for $h \gg d$. It is interesting to note that the $\sqrt{t}$ dependence is maintained with this modified model. We see that r of Eq. (8) can be identified as

$$r_{\text{cap}} = \frac{d - p}{2c \ln(d/p)} \quad (11)$$

Our conclusion, then, is that the capillary radius r obtained from plots of h vs $\sqrt{t}$ is at best a complicated function of both cell diameter and pore size even for

Fig. 22. Model of PS foam structure for wetting data analysis.

Fig. 23. Apparatus for measuring thermal behavior: (a) overview; (b) close-up of sample holder, cryostat, and displacement measuring device.

this simple model, and does not specify either of these quantities. Thus, although our rate-of-wetting data may be useful in certain characterizations of our foams, it cannot give us detailed information about the dimensions of local structure as was previously reported.

Measurement of Thermal Behavior

It is important to characterize the thermal behavior of foam materials at cryogenic temperatures because the foams will be prepared at room temperature and then cooled to approximately 20 K for filling with liquid DT. Our goal was to characterize the dimensional change of foams over a range of 300 to 15 K.

We started the characterization with an existing thermal mechanical analyzer that was designed to operate from 90 to 400 K. The sample is held in a quartz fixture that transmits changes in sample length to a linear variable differential transformer (LVDT). An adjustable force is applied to the sample through an electromagnet. Our modifications to the system included extending the low temperature range to 15 K, which we did by building a new cryostat with simultaneous feedback control of both the cryogen flow and the cryostat heater. We also improved the sensitivity of the length-sensing transducer by substituting an eddy-current transducer for the LVDT. The new transducer has a sensitivity of $1 \mu\text{m}$.

Photographs of the apparatus are shown in Fig. 23. Length changes are

recorded on a chart recorder as well as on a computer, which also controls the cryogen flow. The apparatus can be operated in two different modes: as static length measurement vs temperature, or as dynamic mechanical spectroscopy. In the static length measurement mode, a constant load is applied to the sample and the length is recorded as a function of temperature. In the dynamic mode, a varying force, either square wave or sinusoidal, is applied to the sample in the frequency range of 0.05 to 20 s^{-1} , and the change in length is recorded as a function of temperature. In this mode, changes in the elastic modulus of the foam can be determined throughout the temperature range of the apparatus.

Our first experiments involved measurements of thermal contraction in the temperature range of 300 to 15 K. We prepared the foams by vibratoming them into rectangular prisms with dimensions of 5 by 5 by 7.5 mm. The foams tested were PS, RF, CRF, CA, and silica aerogel.

The fractional dimensional change as a function of temperature is shown in Fig. 24. The contraction of PS foam to 15 K was measured to be 1.4%. We observed exactly the same behavior on samples of full-density PS, which were used to test the operation of the apparatus. Literature values of the thermal contraction of PS are listed as 1.5%. With values of 0.6 and 0.55%, respectively, CA and RF foams have very similar thermal contraction behavior. Silica aerogel and CRF expand on cooling by 0.1 and 0.15%, respectively.

Fig. 24. Results of thermal measurements for low-density foams.

Fig. 25. Development PS hemishell for proposed direct-drive laser ICF target.

The cooling-related expansion of materials having a plate morphology, such as polyethylene, has been observed before.¹⁹ The overall volume of the material decreases with temperature, but the dimensions of the material do not change uniformly: the material contracts strongly in the thin dimension of the plate. This strong contraction causes the length to actually increase. For the purposes of target construction it would be desirable to have no thermal contraction; however, having accurate measurements of the contraction allows us to predict the final dimensions.

From these results, we can conclude that the RF and CRF foams are potentially superior to PS in this respect. However, as mentioned previously, RF foams sometimes fracture during these measurements, which causes problems. The CRF foams do not fracture. Targets can probably be made from PS foams, but the larger thermal contraction may present significant challenges for the target design.

Foam Machining

An assessment of machinability for PS, RF, CRF, and CA foams is under way. We have produced several PS hemishells—such as the one shown in Fig. 25—by simply turning them on a lathe. We are investigating both diamond-point turning and grinding as machining methods, and we have prepared samples of all three foam materials. Methods of quantifying the surface finish using the scanning electron microscope (SEM) are being developed and preliminary results indicate acceptable values. PS foams are by far the easiest to machine, but so far there is nothing conclusive to indicate that the other foams cannot also be suitably machined.

Foam Bonding

We are conducting experiments to identify a suitable bonding agent for PS and RF foams. Several adhesives bond PS foams; these include the GR-650 resin used for silica aerogel, urethane and resorcinol glues, and a plastic resin. It is desirable to use a bonding agent that is mostly C, H, and O or N, rather than the GR-650, which contains silicon and creates a bond of substantially higher density than the hydrocarbon foams. These bonds are being assessed by x-ray radiography and with the SEM.

We have found that only the GR-650 bonds RF foams; none of the other agents mentioned above does. The experimentation is still in its very early stages, however, and we plan to expand the testing to our other foam materials and to test other types of adhesives.

Foam Molding

The required shot repetition rate for a commercial laser ICF facility is estimated to be on the order of 10 s^{-1} . If machining is selected as the method of choice for making the target hemishells, the number of spherical surfaces needed to be machined per day will be well over three million, which appears to be an impractical proposition. Molding offers an acceptable alternative: although molding will not eliminate the need for machining, it limits it to the flat surfaces that will be

bonded. We have therefore undertaken to develop a molding process for PS foams.

Molding of PS foams for ICF targets imposes two apparently conflicting requirements:

1. The material to be molded should have a low viscosity so that it can be poured into the die without trapping air bubbles.

2. The emulsion to be molded should be uniform and have a small cell size.

The way to satisfy the second requirement is to mix the emulsion well, which, unfortunately, increases its viscosity. An immediate consequence of this situation is that simple molding techniques, proven to be useful for many systems, would not work in this case. A low-viscosity emulsion, which fills the die readily without any air bubbles on the

surface, yields a large cell-size, nonuniform foam. A well-formed emulsion, having relatively high viscosity, almost always traps small air bubbles near the surface if one tries to fill a die with it. In injection molding using flow-through dies is also problematic because the high viscosity of the emulsion requires pressure drops well beyond those capable of breaking—at least partially—the well-formed emulsion. A more far-reaching consequence of this dilemma is that any attempts to separate the issues of foam processing and hemishell fabrication are not likely to be very rewarding.

This situation led us to develop an integrated processing/molding scheme, in which the emulsion is created and molded simultaneously. In this technique, the syringes are filled with the

Fig. 26. Schematics of molding apparatus for PS foams: (a) mixer/mold assembly; (b) die assembly.

desired amounts of aqueous phase and organic phase; the die assembly and a specially designed mixing element (described below) are placed between the syringes, and mixing is initiated as described in the earlier articles in this section. Figure 26(a) is a schematic of the mixer/mold assembly. The components of the die assembly are shown in Fig. 26(b).

The original syringe mixer, the PMPY1 described in "Polystyrene Foams" earlier in this article, had to be modified for the molding application. Whenever we assembled the various components of the system air would get trapped alongside the process liquids, leading to bulk and surface imperfections. To eliminate these air bubbles, we modified our operating procedure so that the entire mold-mixer-syringe assembly was fitted together under water and tested for leaks. We also modified the syringe supports so that the completely assembled system could be placed and secured inside them.

To reduce the pressure drop across the mixing orifice and thereby shorten the mixing time while still maintaining

emulsion uniformity, we developed a new mixing element to replace the single orifice. This element (Fig. 27) consists of a perforated plate containing holes of a single diameter. We tried different combinations of hole number and size, and chose a plate with 12 holes of 1-mm diameter.

The die material also imposes some special requirements. The ideal material should be inert toward the emulsion, easily machinable to a smooth surface, and rigid enough to maintain the design dimensions during the molding operation. Metals tend to interact with the emulsion; in the initial experiments with metal dies, the foam surfaces were invariably pitted, pointing to localized emulsion breakup near the die surfaces. Gold-plating the die surfaces in contact with the emulsion proved only marginally useful. Teflon is an ideal material in its inertness, but it is too flexible to maintain dimensional stability. One way around this problem is to use Teflon impregnated with ceramic or graphite, which we have done successfully.

Figures 28(a) and (b) show the hemispherical parts made in the ceramic-impregnated Teflon die, using the new mixer element and the modified syringe pump. The flat surface of the hemisphere has been vibratomed. Figure 28(c) shows the SEM picture of the same hemisphere, showing foam uniformity and cell size. Figure 28 shows that the surface of the part, although mostly uniform, has identifiable nonuniformities. Also, the surface is still not within the target specification of 5 μm . The surface finish of the die, which is similar to that of the foam, appears to be the limiting factor here, but

Fig. 27. Mixing element for PS foam molding apparatus.

Fig. 28. Molded PS foam part: (a) photograph of inner surface; (b) photograph of outer surface; (c) scanning electron micrograph of foam structure. The hemisphere is 1 cm in diameter. ▼

localized breakdown of the emulsion may also cause larger surface defects.

Thus the major problem in molding PS foams at the present time appears to be surface finish. We will attempt to improve surface quality by investigating the causes of local emulsion breakdown, improving the die surface finish by techniques such as diamond machining, grinding, and lapping, and/or by changing the die material to glass.

We have also looked at the feasibility of molding RF foams into hemishells. During the preliminary study, we found that glass molds yield smoother surfaces than metal molds. We have also found that proper sealing is essential to avoid water evaporation during curing. (One way to ensure a good seal is to apply silicone sealant in all the openings of the mold.) We have successfully made hemishells of RF foam from glass tubes and a prototype multi-cavity mold. The surface finish of these hemishells appears reasonably smooth, but they are bigger than the real target size. If molding is chosen as the technique for making hemishells, we will then make a precisely machined glass mold.

Conclusion

At this point, we can compare our foam materials as potential targets. The big advantages of PS over the other types of foams are its superior strength and

machinability and its greater efficiency of production. The fact that it has a larger cell size than the other foams does not seem to be a significant problem in light of the capillary pressure test. However, its relatively large thermal contraction is a significant disadvantage.

RF foams seem to have problems with fracturing under various conditions, but this problem is apparently overcome with carbonization.

None of the foams has actually been quantitated in terms of density uniformity, but since this is almost certainly related to cell size, RF and CRF probably have an advantage here.

CA is not as far along in development as the other foams, but no insurmountable hurdles have been encountered. Needless to say, we have many further tests to perform to confirm that target specifications will be met, but all the foams under development are still promising candidates.

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