Fabrication and Overcoating of Divinylbenzene Foam Shells Using Dual Initiators

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ABSTRACT: Divinylbenzene (DVB) shells with a density of about 100 mg/cc were produced using a dual-thermal initiator system. New high-gain designs for direct-drive ignition at the National Ignition Facility and the OMEGA laser facility at the Laboratory for Laser Energetics require low-density foam shells such as these. Previous research using a single initiator system produced fragile DVB shells that cracked or imploded during the fabrication process. The dual-initiator DVB system used in the present study enabled the shells to be robust enough to produce a high yield of intact shells. The two thermal initiators used were azo-bisisobutyronitrile (AIBN) and another azo-type initiator, V-70. The DVB shells were 800–3500 μm in diameter, with shell wall thickness 7%–10% of the diameter. Because the foam shells were porous, a full-density permeation barrier of poly(vinyl phenol) was developed and deposited on the shells using two techniques to enable the shells to retain gas. The initial results show that the permeation barrier was pinhole free and could hold the gas in a gas-filled shell. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2523–2529, 2006

Key words: DVB foam; foam shells; microencapsulation

INTRODUCTION

Foam shells are required inertial confinement fusion (IFC) experiments at the National Ignition Facility (NIF) in its new high-gain designs for direct-drive ignition. Resorcinol–formaldehyde (R/F) foam shells using this new high-gain design are currently fabricated in a scaled-down version for shots at OMEGA.[1] The diameters of the scaled-down shells must be standard OMEGA size, which is currently 800–900 μm. For the NIF, the shell diameter can range from 2500 to 3000 μm.

The shell wall material and required density of the foam depend on the application for which the shells are to be used. Foam shell specifications for cryogenic shots at OMEGA require a shell wall to be 50–100 μm, with the wall 5%–10% of the shell's diameter. The density of the foam for these cryogenic shots can be in a relatively wide range, 30–150 mg/cc. Because the foam is porous, the foam shells must be overcoated with a pinhole-free permeation barrier to be able to hold the DT or D_2 gas when filled and cooled to cryogenic temperatures. R/F shells have been made with the desired specifications and were the first foam shells to be cryogenically filled and shot in the United States.[1]

In addition to R/F foam, other types of foam materials have been investigated for use in these types of experiments. One such foam is divinylbenzene (DVB). We made DVB shells with the same specifications as the cryogenic R/F foam shells for OMEGA. Like the R/F foam shells, the DVB foam shells required a full-density gas permeation barrier on the outside of the foam layer to prevent evaporation of the D_2 or DT gas when it was cryogenically filled.

DVB foam is a very attractive target material for the inertial fusion energy (IFE) program, which requires an oxygen-free, pure CH foam target.[2] A disadvantage of using DVB is the opaqueness of the shells because of large-sized pores. This opacity precludes visible-light characterization, the current method used to characterize transparent foam and full-density shells. Because of this, new techniques had to be developed to characterize these shells. Possible techniques include the use of X-ray radiography and the characterization of shells while wet in an index-matching fluid, rendering them transparent. Another disadvantage of using DVB is, as shown by a previous work at General Atomics, the brittleness of the shells, which would crack during solvent exchanges and handling, causing a low yield of intact shells. Despite DVB having problems with opaqueness and strength, we decided to investigate how to make its shells more robust and to improve the fabrication of DVB foam shells for the NIF's new high-gain designs for direct-drive ignition.

This article discusses the changes that have been made to the DVB shell production process and how those changes help to make the shells more robust to survive the fabrication process. The issues and results of overcoating the gas permeation barrier of the shells as well as their characterization also are discussed.

EXPERIMENTAL

Fabrication of DVB foam shells

The fabrication of DVB shells was a direct extension of the microencapsulation process of full-density poly(α-methylstyrene) (PAMS) shells.[3,4] The shell diameter and shell wall produced were controlled by producing shells with a triple orifice droplet generator.[1–8] The shells could be made via the microencapsulation process because the shells were made using a typical water/oil/water microencapsulation system.[3,4] Because this process is similar to the process for producing PAMS shells, we did not make many changes to our current droplet generator design. The DVB monomer (Aldrich, USA) was dissolved in an oil solvent such as dibutylphthalate (DBP; Aldrich) along with an initiator or initiators. The droplet generator produced shells by using the oil-based DVB solution to encapsulate a drop of water. This oil/water emulsion was then stripped off the encapsulation needles using a water-based solution, and the shells were stabilized between the water droplet and the water-based solution. The shells were then placed in a water bath at the initiator activation temperature. At this temperature the initiators formed free radicals and initiated polymerization, which in time gelled the DVB/DBP solution, forming DVB foam shells.

A previous investigation of the production of DVB shells used one thermal initiator, azobisisobutyronitrile (AIBN; Aldrich),[2] at 50°C, which initiated free radicals that started polymerization of the DVB foam solution. When this process was used to make DVB foam shells by the microencapsulation process, many shells cracked or imploded during the solvent exchange process (Fig. 1). Shells produced in the current study such as PAMS and R/F shells did not show this problem.

In some polymer systems, a combination of initiators has a synergistic effect on the system, which can affect the physical properties as well as the polymerization time of the polymer. These synergistic effects are seen only when a combination of initiators, not a single initiator, is used. Because of this, we combined AIBN with another azo-type thermal initiator, 2,2′-azobis-4-methoxy-2,4-dimethylvaleronitrile (V-70; Wako Chemicals, USA), in the DVB/DBP solution. We hoped that using the combination of these two initiators would produce DVB foam shells robust enough to survive, thus producing a high yield of intact shells.

V-70 initiates free radicals at a lower temperature (~30°C) than does AIBN (50°C). The DVB shells were
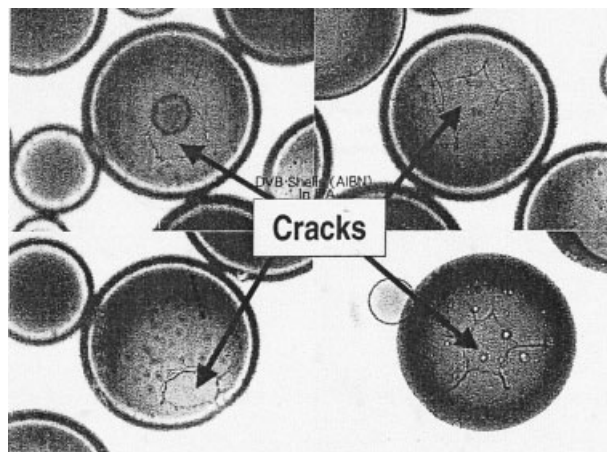
Figure 1 DVB shells of 2 mm made with a single initiator (shells cracked during solvent exchange). The cracking of shells during the solvent exchanges yielded fewer intact shells.

made using the W/O/W microencapsulation process. Because the two initiators initiate free radicals at different temperatures, we started the polymerization of the shells at 38°C. At this temperature the shells were more closely density matched, which allowed the shells to center better, yielding shells with good wall uniformity and lower nonconcentricity. Because V-70 started to form free radicals at about 30°C, heating the solution to 38°C ensured that free radicals were being formed. When the V-70 broke down to form free radicals, it attacked the two reactive vinyl groups of the DVB, making them unstable and causing the DVB monomers to crosslink with one another. As more and more crosslinking occurred, the DVB solution started to polymerize, forming DVB foam. Because oxygen can inhibit the polymerization process, a nitrogen line was run into the rotoflask to remove any oxygen. At this temperature, the V-70 should have been used up, causing the DVB shells to start to gel and to start to become white and opaque. Because AIBN initiates free radicals at a much higher temperature and its half-life at 38°C is longer than 24 h, some or most of the AIBN should have remained stable in the DVB solution. At this point the temperature of the water baths containing the shells was increased to 70°C, allowing the AIBN to initiate free radicals, which would crosslink with any DVB monomers that not yet crosslinked, thus acting as a postcure process for the DVB shells.

After the shells were cured and had gone through the postcure, they were washed with water to remove the PAA and then, to exchange the solvent, placed in isopropyl alcohol (IPA) to remove the water and DBP in the shell. Exchanging the solvent in IPA, whether directly or gradually, did not crack the shells or cause them to implode. The results for the shells surviving the solvent exchange in IPA are shown in Figure 2. The yield of intact shells after IPA exchange was about
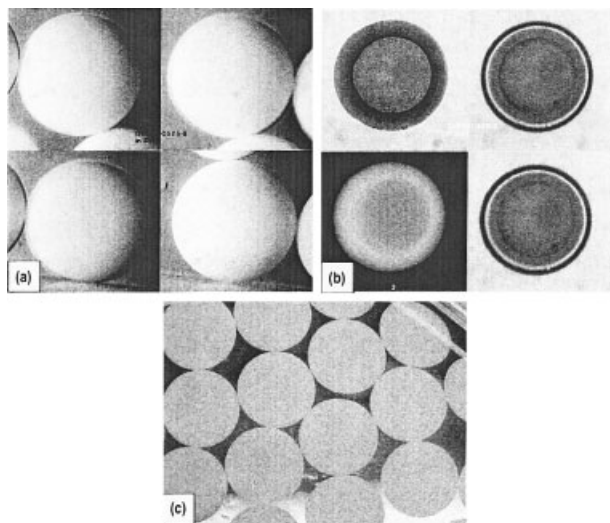
Figure 2 Microscopic images of 3.5-mm DVB shells made by a dual-initiator DVB process (no cracking), leading to a higher yield of intact shells: (a) individual 3.5-mm DVB shells; (b) shells in an index matching fluid; (c) a group of DVB shells.

95%. The dual-initiator system helped to strengthen the DVB shells so that they could complete the IPA exchange without cracking or imploding, greatly improving yield as compared to that produced with the single-initiator system.

PVP overcoating of DVB shells

A key requirement for these foam shells was an overcoat of a full-density gas permeation barrier. The process used to close the R/F foam pores was to apply a polymer coating through the glow discharge polymer (GDP) process.[1,8,9] This could not be applied directly on the DVB foam shells because the DVB pore size was too large for the GDP to fill. Another approach that we used was to overcoat the DVB shells with poly(vinyl phenol) (PVP; trade name Maruka Lyncur-M, from Chemiway-Maruzen Petrochemical, Japan) through an interfacial polycondensation reaction.[1,10] PVP that had been overcoated on R/F foam shells was shown to hold gas in the R/F foam shells.

The DVB shells made with the two-initiator system survived the water-to-IPA solvent exchange. In addition to this solvent exchange, the DVB shells needed to survive another solvent exchange for the shell to be coated with a gas permeation barrier. The first step in the PVP overcoating process was the solvent exchange of the shells from IPA to diethylphthalate (DEP; Aldrich). The results showed that the shells survived the exchange into DEP without cracking or imploding.

After surviving the 6- to 7-day solvent exchange from IPA to DEP, the DEP solution was removed, and the DVB shells were exchanged in a 0.10 mmol isophthaloyl dichloride (IPC) solution dissolved in DEP.

The DVB shells remained in this solution for 2–3 h, allowing the IPC solution to saturate the surface of the DVB shells. The shells were then washed with 5 wt % poly(vinyl alcohol) (PVA) in order to remove excess oil on the DVB foam surface. Next, the shells were added to a beaker of 1.5 wt % hydroxyethyl cellulose (HEC; Polyscience, USA) solution containing 0.50 wt% of a surfactant such as Tween 80, which prevents DVB shells from sticking to one another. A stir blade attached to an impeller was put into the beaker in order to stir the solution at about 300 rpm and suspend the shells. Next, a 0.1 mmol PVP solution containing water and 0.10 mmol NaOH was added to the HEC solution with the DVB shells. In the PVP solution the NaOH attacked the hydroxyl group of the PVP (R-OH + NaOH $\rightarrow$ R-ONa + H_2O). The pH of the solution was crucial to the reaction. If the pH was less than 11, the IPC could crosslink with the HEC or PVA in the solution and not the PVP. But at a pH of 11–12, the IPC would only react with the PVP, not the HEC or PVA, in the solution. When the PVP solution was added to the HEC solution containing the DVB shells, the ONa group of the PVP attacked the Cl groups of the IPC that was absorbed on the foam surface. This resulted in PVP crosslinking with the Cl groups of the IPC that was attached to the DVB foam shells. NaCl was produced as a byproduct. It formed a uniform PVP overcoat around the DVB shell. In previous work on R/F and other foams that were PVP-overcoated by an interfacial polycondensation reaction, the coating rate was found to be roughly 1 μm/min. Interfacial polycondensation is a self-limiting reaction that slows after the deposition of around 10 μm of coating.

To create a 5-μm PVP overcoat, we coated the shells for 5 min, after which they were removed from the PVP/HEC solution and washed 5 times with 1 L of DI water. This removed any NaCl and HEC from the shells. The shells were then washed in a 10% HCl solution for 5 min to remove any PVP and Na that had not reacted with the IPC on the DVB shell surface. The shells were washed again with DI water to remove the acid and were then solvent-exchanged back into IPA for 6–7 days to remove any water, oil, and IPC. Finally, the shells were dried in a CO_2 supercritical dryer. Figures 3 and 4 show SEM images of a DVB shell overcoated with PVP and its cross section, respectively. A high yield of shells (~95%) survived the PVP-overcoating process without cracking or exploding.

RESULTS AND DISCUSSION

Wall uniformity

Like any other ICF spherical target, DVB shells must be accurately characterized for wall thickness and uniformity, diameter, and nonconcentricity. Current production shells such as R/F and PAMS are transparent
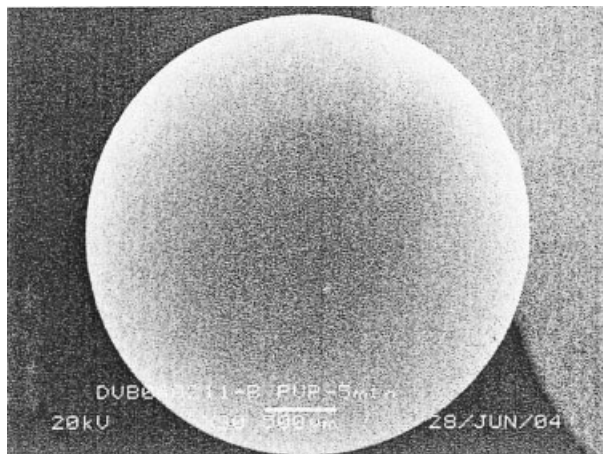
Figure 3 SEM image of a DVB shell overcoated with PVP.

so that visible characterization can be performed. DVB shells are opaque, and thus visible characterization can not be done. Because of this, we developed wet characterization as another way to characterize these shells. This was done by placing the DVB shells in an index-matching fluid. DVB has a refractive index of 1.5–1.6. IPA has a refractive index of about 1.1. Because of the lower refractive index of IPA, the DVB appeared opaque. If the DVB shells were in a fluid that had the same refractive index, the shells would appear transparent. Benzyl salicylate was used as the fluid to measure DVB shells.[11] When we put our DVB shells in this fluid, the shells became transparent, allowing us to measure the shell wall and its uniformity.

Wet characterization is also used as a screening process for R/F shells, and a wet characterization procedure to measure diameter, wall thickness, and uniformity of the R/F shells in IPA exists. Because of this, we adopted this technique to measure the DVB shells in an index-matching fluid, instead of IPA. The statistical wall uniformity results of several batches of DVB shells (Fig. 5) showed that a majority of the shells had non-concentricity (NC) of less than 5% or a delta wall of less than 10%, which were the standards adopted for wall thickness uniformity and delta wall, respectively. As an alternative, X-ray radiography may be used to characterize DVB shells because it can
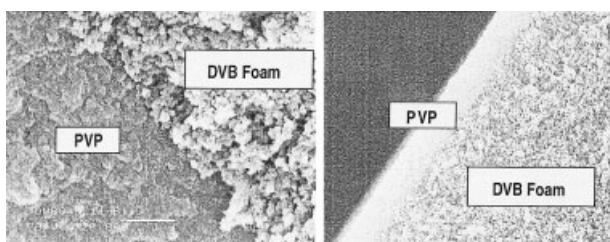
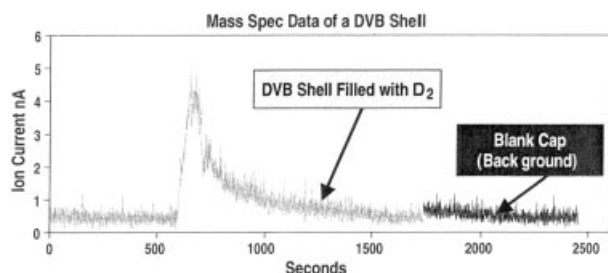determine shell diameter, wall thickness, and wall uniformity in dried shells.

PVP overcoating results

The PVP-overcoated DVB shells were tested for gas retention by permeation filling the shells with argon and observing the argon content of the shells versus time by tracking the argon X-ray microfluorescence (XRF) signal. This same procedure was used to test the R/F shells for gas retention.[1] This procedure did not work for our large DVB shells (3–3.5 mm) because there was so much interference from the foam, causing scattering of other influences that interfered with detecting the argon signal. This interference from the DVB foam made it difficult to detect the argon remaining in the shells.

Because of this interference we used a mass spectrometer (MS) to try to detect the argon leakage. A PVP-overcoated DVB shell was permeation-filled with argon. The shell was placed in a sample holder and connected to the MS. The volume surrounding the shell in the MS was evacuated and then opened to the gas detector. The initial spike and subsequent decay of the argon signal showed that argon was being measured. The half-life of argon in the shells was about 14 min. Because we believed the MS signal may have been affected by the approximately 1% argon concentration in the air, we also performed the MS analysis with D_2. Because there was no D_2 in air, any signal detected would be from D_2 permeating the shell. As shown in Figure 6, the shells were also found to hold D_2. The half-life obtained for D_2 in the DVB shells was about 70 s. This result shows that the gas did not leak out of the shells instantaneously and that the PVP coating was pinhole free around the foam shells, resulting in their being able to fill with and retain gas. But whether this decay of D_2 gas in the shells wa sufficient to fill the shell cryogenically still needed to be tested. Being able to detect Ar and D_2 signals from the shells was encouraging that our PVP overcoat could be gas retentive. The yield of gas-retentive shells was 5 of 10, similar to that for R/F shells. More testing

Figure 4 SEM image of a cross section of a PVP-overcoated DVB shell.
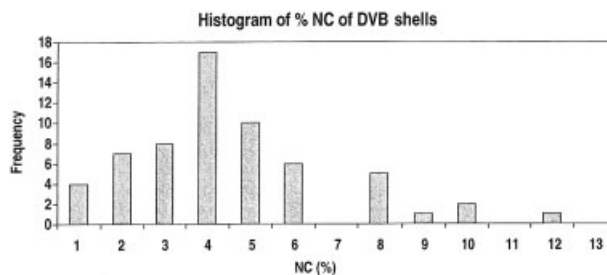
Figure 5 Histogram of shell-wall nonconcentricity of the DVB foam shells showing that a majority of the shells met wall uniformity specifications and had NC values of 5% or less.
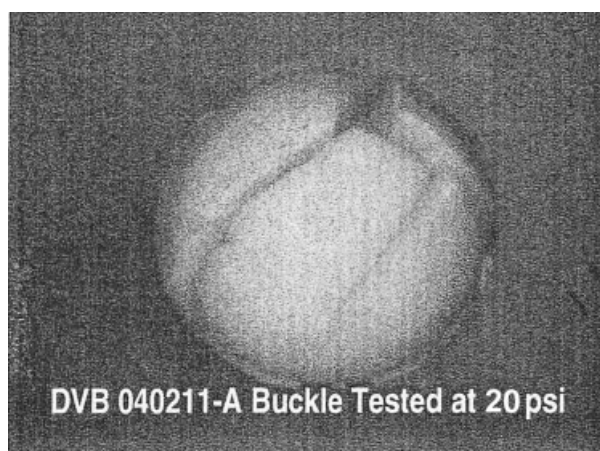
Figure 6 MS data on gas retention of the PVP-overcoated DVB shells.

Figure 8 Photograph of another overcoated DVB shell from the same batch as that shown in Figure 7. This shell did not appear to buckle or crack when buckle tested, and it tested at pressures from 10 to 98 psi. But when examined closely micro-cracks where seen.

of these PVP-overcoated DVB shells must be done to verify these results.

The shells also were buckle-tested by being overpressurized in a pressure cell and then the pressure at which they failed being observed through a window. The shells tested held gas with a diameter of 3.5 mm. The shells did not implode catastrophically at 20 psi; at this pressure cracks could be seen (Fig. 7). Shells were then tested at 10 psi. At this pressure nothing was observed in the window, but when examined under a microscope, small microcracks could be seen. Other shells were tested at 98 psi; some of these did not appear to crack or buckle as observed through the viewing window (Fig. 8). But like the shells at 10 psi, when observed under a microscope, microcracks were observed. Because the shells were opaque, we could not tell if the shells developed microcracks at that pressure or at a lower pressure. More buckle strength testing of these shells must be done in order to understand the limits of the strength of these shells.

PVP/GDP overcoating

It was observed that the PVP-overcoated DVB shells were smaller after being dried than when they not


Figure 7 Photograph of an overcoated DVB shell after buckle testing at 20 psi. Unlike the other overcoated R/F foam shells and the thin CH shell, this shell did not buckle catastrophically.

coated (dried or in IPA). The shell total diameter of the DVB foam appeared to have shrunk. This shrinkage of the DVB foam was observed after the overcoat was applied and the shells were exchanged into IPA. This also was observed when the R/F shells were coated with PVP.[1] We found that the R/F foam shrunk by about 20% for a PVP thickness of 3 μm or higher. This amount of shrinkage could cause densification of the foam, making it difficult to determine the density of the foam. This is why PVP was not chosen as the gas permeation barrier overcoat for the R/F foam shells.[1] The DVB shells shrunk by about 13% for a PVP thickness of 5 μm. This is still enough to make densification of the DVB foam a concern. From the PVP overcoating on R/F foam it was shown that with a thin coating, 1–2 μm, of PVP, shrinkage of the foam layer was negligible. Because of this, we attempted to coat the DVB foam shells with a layer of the same thickness, 1–2 μm, in order to minimize shrinkage. Initial results showed that negligible shrinkage of the DVB foam could be achieved with a thin flash coating of PVP. However, it did not provide an adequate gas permeation barrier. Because PVP is a full-density polymer that overcoats DVB foam shells evenly, the shells could now be coated with a plasma polymer. The DVB shells could be coated with 3 μm of GDP so that the total full-density overcoat would be 5–6 μm. This would solve the problem of the shrinkage of DVB foam from PVP overcoating and might provide an adequate gas permeation barrier for DVB foam shells.

For the first flash coating of these shells with PVP, we used the previous coating rate of about 1 μm/min. We wanted the thickness of the coating to be about 2 μm. Because of this, the DVB shells were separated into a batch coated for 1 min and a batch coated for 2 min. No noticeable shrinkage was found for either overcoat. The observed thickness of the PVP coating
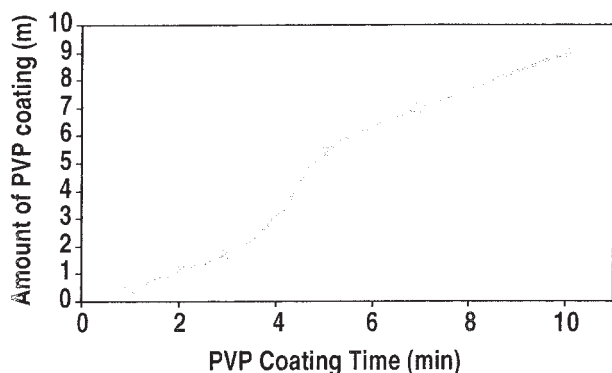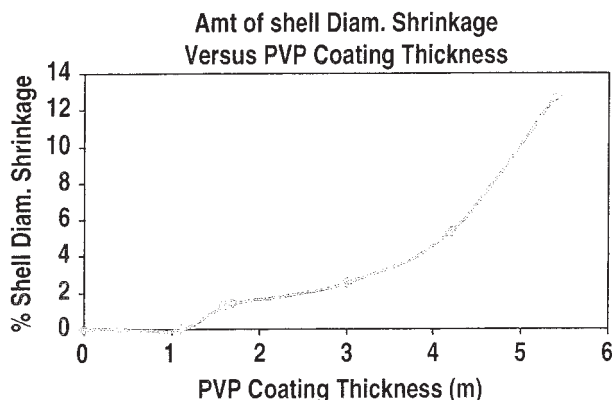
Figure 9 Amount of PVP coated on the DVB shells over time, which was not a linear process.
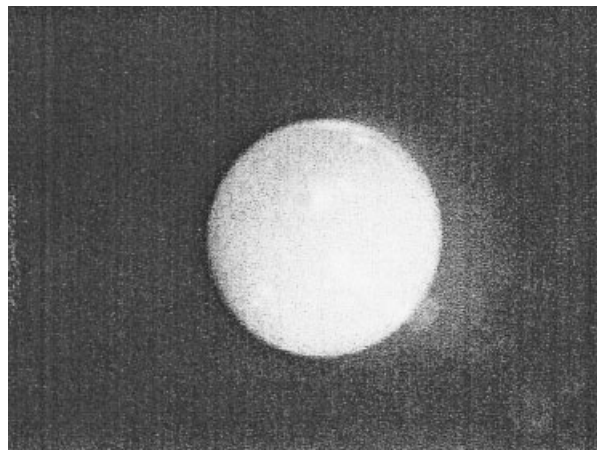

Figure 11 Picture of a 900-μm PVP/GDP-coated DVB shell.

thickness was not what was expected. The 1-min coating had a PVP thickness of about 0.40 μm, whereas the 2-min coating had a thickness of 1 μm. Both were measured with an interferometer. The varying thickness of the resulting coats shows that the coating rate was not constant (1 μm/min). The amount of PVP overcoating over time, illustrated in Figure 9, shows that the coating rate was not linear, both increasing and decreasing over time. The graph also shows that the coating rate increased to a certain point and then started to decline because the polycondensation reaction is a self-limiting reaction.

We also measured shrinkage of these shells. We saw no or minimal shrinkage (0%–2.5%) with a PVP coating of 3.5 μm or less. This is similar to our findings for the PVP overcoating of R/F foams. With PVP coatings of 4–5 μm, shrinkage can be about 13%. To minimize shrinkage of DVB shells from overcoating with PVP, we could coat no more than 3.5 μm of PVP. Figure 10 shows the amount of shrinkage versus amount of PVP overcoat.

DVB shells were coated with 0.5, 1, 1.5, and 3 μm of PVP and then coated with 3 μm of GDP as well as 5–6

μm of GDP. Figure 11 shows a picture of a DVB shell overcoated with PVP/GDP. It can be seen that the coating is smooth and uniform and contains no cracks. Figure 12 shows a SEM image of a cross section of a DVB foam shell coated with PVP and GDP.

The shells were measured for gas retention by XRF, which showed that the 900-μm-OD DVB foam shells did not cause as much background scatter as did the larger DVB foam shells. To confirm these results, shells also were tested on the mass spectrometer with D_2 as the surrogate gas. It was found that about 80% of the shells with a 4- to 6-μm GDP overcoat were gas retentive, compared to only 50%–60% of the 3-μm-thick overcoated shells. The thickness of the PVP coating did not greatly affect the yield of gas-retentive shells when the PVP coat was $\leq$ 1μm. The GDP overcoating enabled the shells to have a barrier to permeation. Figure 13 shows the XRF data on gas retention of DVB shells coated with the PVP/GDP permeation barrier. The plot shows the number of Ar signals
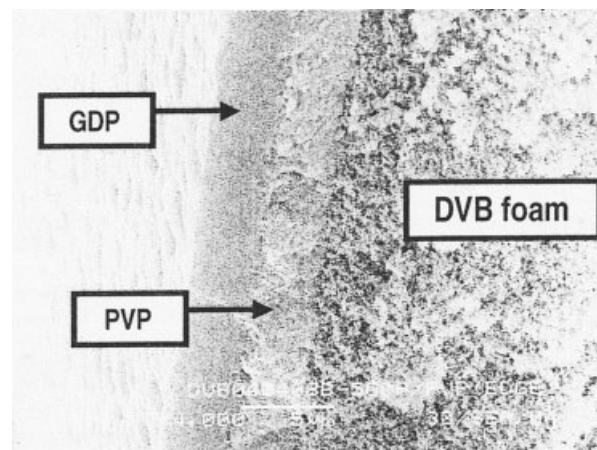

Figure 10 Amount of shell diameter shrinkage versus PVP coating applied. Shrinkage increased with increases in the amount of PVP applied to overcoating the shell.
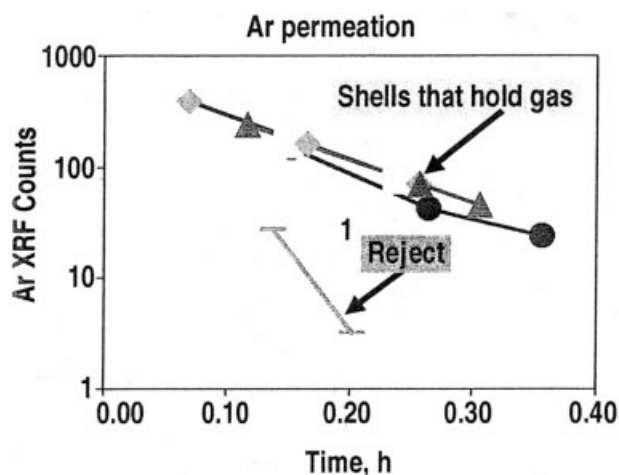

Figure 12 Cross section of a PVP/GDP-overcoated DVB shell.

Figure 13 XRF data on gas retention of DVB shells overcoated with PVP/GDP. Shells holding gas showed gradual decay of Ar (pinhole-free coating), although the rejected shell, which did not hold gas, decayed more rapidly.

detected from the shells over time. Gradual loss of Ar from the shells shows that the overcoat was pinhole free because the gas did not escape the shells instantaneously. The plot also shows data from a shell that did not hold gas. In that plot the number of Ar signals from the shell was much lower at the beginning than was that from shells that held gas. The decreasing Ar count rate was orders of magnitude faster than the gas-retentive shells, suggesting that gas was leaking through pinholes or cracks. The gas-retentive shells were then sent to the Laboratory for Laser Energetics, where they are to be tested for cryogenic filling and layering.

CONCLUSIONS

DVB shells were fabricated using the new dual-initiator approach. This new approach made the DVB shells more robust to survive solvent exchanges; the interfacial polycondensation reaction of the PVP overcoating and drying of the shells in a supercritical CO_2 dryer yielded about 95%. The resulting DVB shells could be produced with a difference in wall thickness of less than 10% and delta walls of 10% or less. We also successfully overcoated a pinhole-free gas permeation barrier on the DVB shell with PVP via interfacial polycondensation reaction, followed by 3 μm of a plasma polymer coating (GDP). This dual permeation barrier was tested by the XRF and MS techniques and found to successfully hold gas. These shells still need further testing to see if the permeation barrier is suitable at cryogenic temperatures to allow D_2 liquefaction and ice layering. Finally, more work must be done on the gas retention and buckle strength of these shells.

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