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**THE USE OF CaCl_2 AND OTHER SALTS TO IMPROVE
SURFACE FINISH AND ELIMINATE VACUOLES IN ICF
MICROENCAPSULATED SHELLS**

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THE USE OF CaCl_2 AND OTHER SALTS TO IMPROVE SURFACE FINISH AND ELIMINATE VACUOLES IN ICF MICROENCAPSULATED SHELLS

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ABSTRACT

Polystyrene and poly(α -methylstyrene) (PAMS) shells made by microencapsulation are prone to having vacuoles in the walls and a concomitant surface roughness. These defects can be detrimental to the implosion required for ICF shots. We have found that adding sufficient salt (typically CaCl_2 or NH_4Cl) to the exterior polyvinylalcohol (PVA) solution during the drying phase inhibits the formation of vacuoles and decreases the surface roughness of the shells. The use of such salts does affect other shell specifications, for which other process variables must be adjusted.

I. INTRODUCTION

ICF targets require a high degree of spherical perfection and compositional uniformity in order to obtain high quality implosions. Microencapsulated polystyrene shells used in the past usually had a high number of vacuoles in the shell wall, which could be sources of Rayleigh-Taylor instabilities. With the use of the PAMS/GDP process (PAMS = poly(α -methylstyrene), GDP = glow discharge polymer) to make shells, the PAMS shells had a much worse vacuole problem. The vacuoles in the wall of the PAMS were initially considered irrelevant, since the PAMS is decomposed and removed to leave the GDP shell.¹ However, the PAMS vacuoles also lead to a surface roughness which is patterned on the internal and external surface of the GDP shell. Thus, a way to eliminate the vacuoles in PAMS, as well as polystyrene, was required.

The prevailing understanding of the vacuole formation is that water from the interior water (W1) and exterior water/PVA (W2) diffuses into the polymer oil

phase (O1, 11 wt% PAMS in fluorobenzene). Upon removal of solvent, the remaining solvent becomes supersaturated in water and nucleates a water droplet. Upon shell wall curing and W1 extraction, the water in the droplet is removed, leaving a vacuole in the shell wall.

The above understanding cannot be entirely correct. Adding a drop of O1 to a solution of W2 in a sealed vial results in a cloudy O1 drop. The cloudiness indicates the presence of a second phase—the water droplets in the O1. The “water droplet” is nucleating in the absence of supersaturation driven by solvent removal. An alternative interpretation is that the “water droplet” has a water activity lower than that of the W2 phase. The water would prefer to form a droplet in the O1, than be in the W2.

To eliminate the vacuole formation, it seemed reasonable to find a way to limit diffusion of water into the O1. This approach seeks to make water want to stay in the water phase, and not move into the O1 phase. In a thermodynamic sense, the activity of the water phase W2 must be reduced. The simplest way to reduce the water activity would be to add salt to the W2 solution. This addition lowers the water vapor pressure, a measure of the water activity. Very few salts are compatible with a PVA solution. However, CaCl_2 and NH_4Cl are two such salts which are compatible with the W2 PVA solution.

To demonstrate this thermodynamic understanding, a drop of O1 was added to a solution of W2 in a sealed vial, and allowed to become cloudy overnight. A salt solution was then added to the W2 phase, and the O1 droplet cleared. The clear droplet indicates the second phase material—the water droplets—have been removed or significantly reduced in size.

II. EXPERIMENTAL RESULTS

In an initial set of experiments with CaCl_2 , solutions from 0.5 to 3.0 wt% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ were made in the W2 PVA solutions. Typically, 75 cc of a 20 wt% salt solution was added to one liter of W2 solution containing the newly encapsulated PAMS compound shells, to make a W2 solution of 1.5 wt% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. After the typical 6 hour cure time, the dried shells were washed and extracted. Even at this point before washing, the improved optical clarity of the shell was obvious. A series of photos of such dried shells shows that vacuoles are still present at 0.5 wt%, but are clearly gone by 1.5 wt% (Fig. 1). We subsequently standardized on 1.5 wt% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

In a second set of experiments, an NH_4Cl solution was added later and later to a series of beakers during the curing time. Up to about 1.5 hours, the NH_4Cl solution can apparently collapse any droplets which have formed by pulling the water out, and the shell wall can collapse the droplet region. However, after 1.5 hours, the shell wall cannot collapse around the droplet region and/or the water cannot diffuse out as quickly since the shell wall is growing more viscous and hard. Our current process for making shells adds the salt solution about 1 minute after the shells are placed in the curing bath.

Figure 2 shows the change in the amplitude of the surface roughness modes of the PAMS shells, over various ranges, upon addition of salt. The AFM spheremapper power spectrum is broken into several regions, and the region mode 50–200 (sizes 59–15 μm diameter) is consistently reduced upon adding salt. The consistent reduction of any region of the power spectrum is a significant improvement in the shell quality.

The addition of salt to eliminate vacuoles has two unintended consequences. First, we consistently found some Ca and Cl in energy dispersive x-ray analysis of particulates found on the inside. These particulates are found in the shells even when the CaCl_2 solution is added even an hour or more after the wet shell is made. We can only ascribe these particulates as coming from diffusion of CaCl_2 across the shell wall to the interior. These particulates remain in the GDP shell after pyrolysis, and thus are a source of undesired high Z impurities in the implosion. We have replaced the CaCl_2 solution with NH_4Cl solution (still 1.5 wt%), since any ammonium chloride which may diffuse into the interior will decompose and be removed during the pyrolysis.

A second major consequence upon adding salt, was a change in the shell sphericity. Omega sized shells (circa

940 μm o.d.) had typically been out-of-round by about 0.5–0.7 μm . (Out-of-round is taking a single image of the shell, and fitting an ellipse to the image, and taking the difference between the major and minor axis as the out-of-round.) Upon using 1.5 wt% CaCl_2 addition, the shell out-of-round increased to 2–4 μm from batch batch (see Fig. 3). Ultimately, we found that the increased out-of-round results from the change in the W2 solution density. The out-of-round measure is significantly determined by the density mismatch between the W2 and O1. At the 60°C temperature of curing, the density mismatch for PVA/water W2 with the O1 was minimal. Upon adding CaCl_2 (or ammonium chloride), the density mismatch at 60°C was larger. We found that reducing the bath curing temperature to about 43°C for 1.5 wt% CaCl_2 (or 48°C for 1.5 wt% NH_4Cl) gave a better density match to O1, and the out-of-round returned to near 0.5 μm .²

The control of water diffusion into the shells by use of salt solutions to eliminate vacuoles is controlled by the difference between the water activity of the W2 versus the water activity of the water in the vacuole state. If the water activity in the W2 is greater than that of the vacuole state, then water will diffuse into the shell wall and form a droplet. In pure PAMS/fluorobenzene, the vacuole state activity lies below the activity of pure water/PVA, but above the water activity for 1.5 wt% CaCl_2 or 1.5 wt% NH_4Cl .

Adding salts to the W2 has been shown to reduce and eliminate the number of vacuoles. However, the water activity of the O1 phase can be lowered further by hydrophilic impurities in the O1, which can lead to formation of vacuoles in spite of using salts in the W2. For instance, the starting PAMS we receive from the supplier is made from butyl lithium, and thus some lithium methoxide is present in the PAMS. The PAMS is routinely dissolved and reprecipitated before use, which removes this lithium methoxide (and lithium hydroxide). We found that if this reprecipitation/purification step is not taken, the salt solution does not entirely eliminate vacuoles. If the lithium methoxide is present in the O1 when the shells are made, it will draw water to itself to make a concentrated lithium hydroxide solution in the shell wall, and vacuoles will be formed. The starting PAMS must be reprecipitated to eliminate impurities. A second potential source of impurities is the fluorobenzene used as the O1 solvent. We initially used 99% fluorobenzene (Aldrich) straight from the bottle. We later found evidence of KCl particulate in the fluorobenzene. If any KCl particulate got into the O1 shell wall, it would pull water to itself, and form a vacuole. We now distill the fluorobenzene before use to remove this source of impurity.

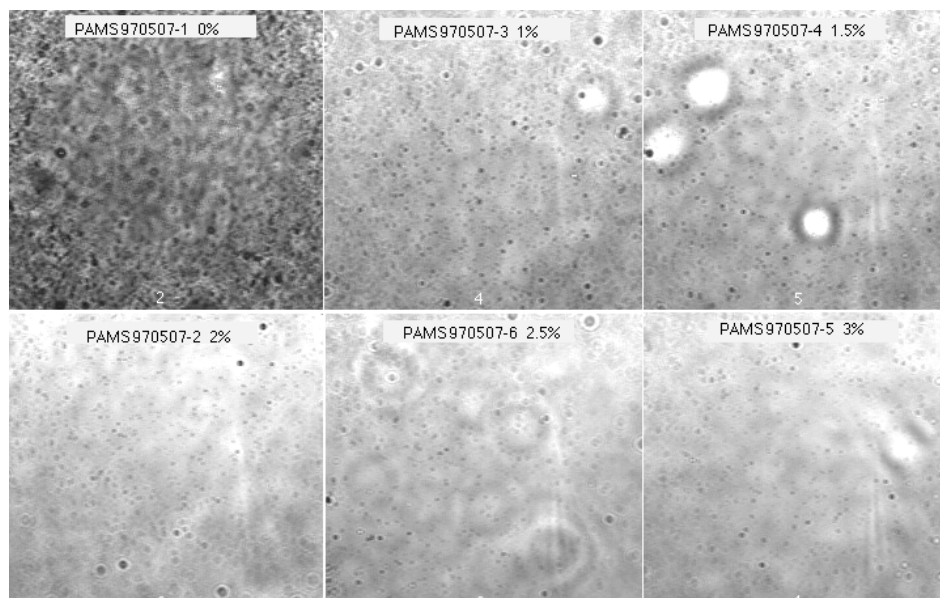


Fig. 1. A series of dried shells made using a variable amount of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ solution. W2 solutions using 1.5 wt% or greater result in no vacuoles.

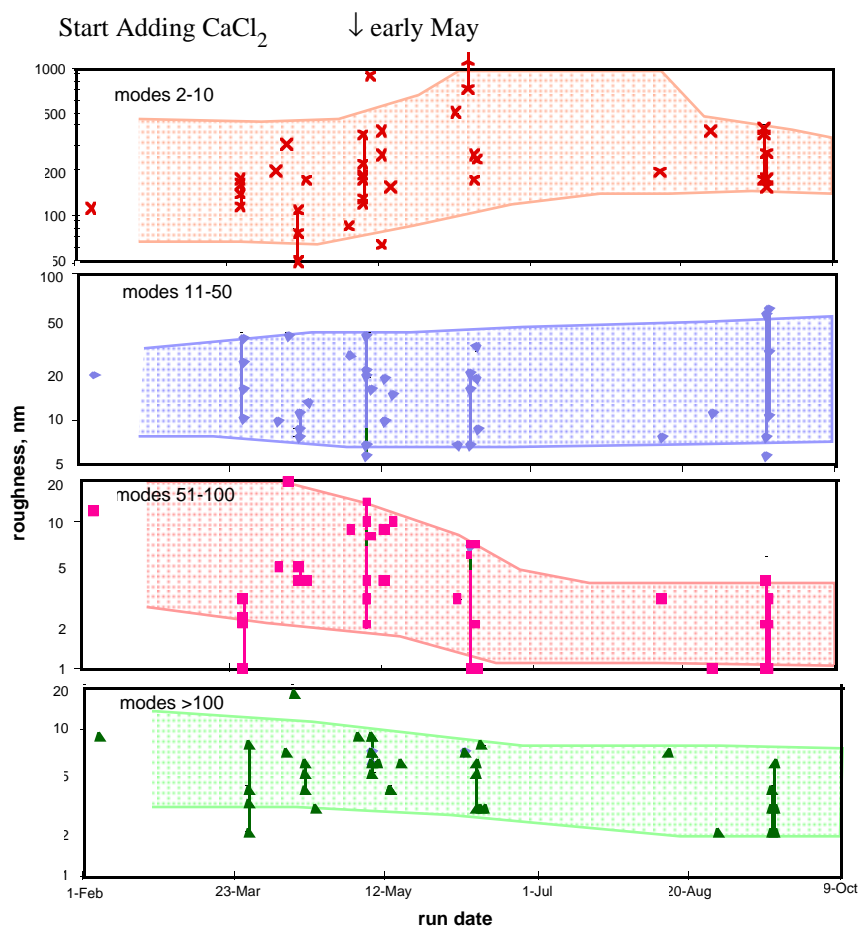


Fig. 2. A plot of the AFM spheremapper mode region amplitudes, both with and without adding CaCl_2 . The mode region 50–200 shows a consistent reduction in amplitude.

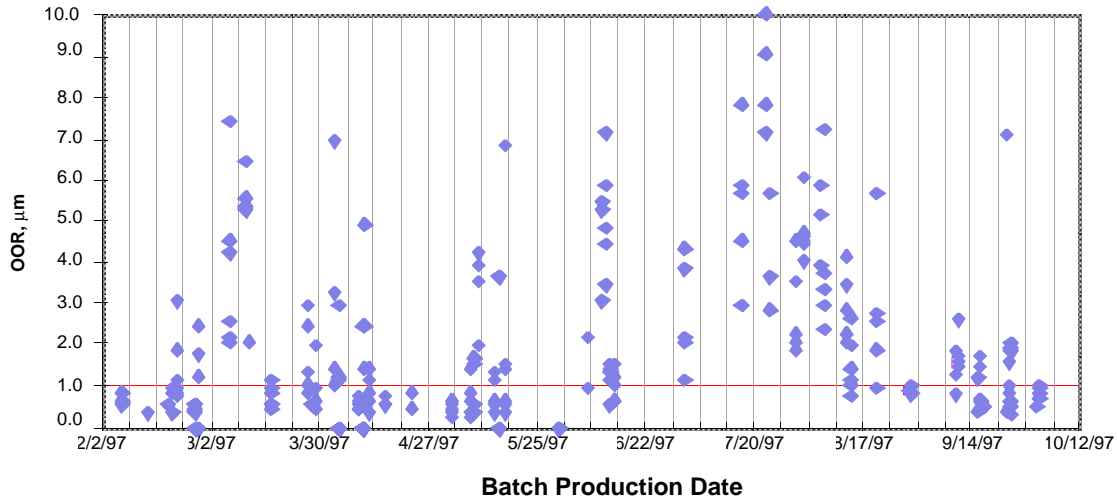


Fig. 3. A plot of the shell out-of-round over time. Before May 1997, the shells were cured without salt at 60°C. After early May 1997, the out-of-round increased when CaCl_2 was added for a cure at 60°C. After September 1997, the out-of-round decreased while using CaCl_2 when the curing temperature was reduced to 43°C.

III. CONCLUSION

The longstanding problem of vacuoles in micro-encapsulated shells for ICF purposes has been solved by judicious use of salts in the W2 phase. Ammonium chloride is the current salt of choice. Removal of other sources of impurities in the O1 solution is also required.

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