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**MICROENCAPSULATION PROCESS FACTORS
WHICH INFLUENCE THE SPHERICITY OF
1 mm o.d. POLY(α -METHYLSTYRENE) SHELLS
FOR ICF**

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ABSTRACT

We have identified three process variables which determine the sphericity of polymer shells made by dual orifice microencapsulation. 1) The density mismatch between the outer aqueous solution and the polymer oil phase must be minimized. We have minimized this density mismatch by adjusting the water bath temperature. 2) The stir rate has an effect, with a minimum non-sphericity located near 50–70 rpm stir rate. 3) The outer aqueous solution must have enough total oil solvent (fluorobenzene in the drops) to be beyond the aqueous saturation level (1.5 g/l) at the beginning of the solvent extraction. Using the optimal conditions for a 1000 μm o.d. shell, we produce a minimum variation in the radius of a given shell, in the neighborhood of 0.4 μm .

I. INTRODUCTION

For an ICF spherical target to have optimum uniform implosion performance, the shell target must be as spherical as possible. In the PAMS/GDP process,¹ the initial PAMS mandrel shell is critical in producing spherical targets—if the PAMS shell is not spherical, then later coatings will also be non-spherical. Producing the required sphericity (or out-of-round, OOR) becomes more and more difficult, as the target diameter increases from 0.4 mm (Nova) to 1 mm (Omega) to 2–3 mm (NIF). For Omega shells discussed here, the specification for OOR on the final target shell is less than 3 μm . This specification sets a maximum tolerable OOR on the PAMS mandrel of less than 1 μm OOR. OOR is defined as $(d_{\text{max}}-d_{\text{min}})/2$, and 4π OOR is defined as $\sqrt{2}$ OOR.

The dual orifice microencapsulation process involves making liquid compound drops in a droplet generator.¹ An inner drop of water (W1) is surrounded by a oil drop (O1) composed of an 11 wt% PAMS (400 K MW, Scientific

Polymer Products) in fluorobenzene (99%, Aldrich). The drop is formed by syringe pumps sending the solutions through a dual orifice needle, at typical flows of O1 and W1 of 50 cc/hour each (50/50 O1/W1). The drops are stripped off the needle by aqueous PVA solution (W2) (0.2 wt% PVA, 25 K MW, 88% hydrolyzed, Polysciences) flowing at about 250 cc/minute. This process makes Omega shells at about 2000/minute. The compound drops in W2 flow down a collection tube into a one liter beaker. When filled to one liter, the beaker is removed to a curing water bath, and the solution is stirred for 6 hours. The fluorobenzene leaves the O1, leaving a PAMS shell wall surrounding the W1 interior drop. The solvent free shells are collected, washed, and the interior water is extracted, to yield the final PAMS shells.

The dual orifice microencapsulation process is deceptively simple, with few process variables. However, these variables influence each other, so a change in one variable modifies the shell parameters associated with other variables. For example, a change in the water bath temperature effects the time for solvent removal, the solubility of the oil solvent in the aqueous phase, the densities of each phase and the density mismatch, the viscosities of the solutions, and the interfacial surface tensions involved in making the droplet spherical. Thus, one process variable (bath temperature) can effect many factors which impact the final shell properties. In this paper, we delineate three key process variables which impact the shell sphericity.

II. RESULTS

A. DENSITY MISMATCH

When we began to make encapsulated shells in the droplet generator, we used fluorobenzene, rather than the

previous binary solvent system, benzene plus 1,2 dichloroethane, in order to have a solvent system which stays at the density of the water phase throughout the extraction. We began with a 60°C curing water bath, and we were producing Omega shells with an OOR of less than one μm , within the specification. However, the walls of those shells were loaded with vacuoles, which were undesirable. We found that upon addition of CaCl_2 to the W2, we could prevent the formation of vacuoles if the final $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ concentration in the beaker was 1.5 wt%.² However, from that point, the OOR of the shells became 2–4 μm , well above the <1 μm specification (see Fig. 1).

Bob Cook had estimated that the maximum OOR of a simple liquid oil drop should look like

$$\text{max OOR} = g(\Delta\rho/\gamma)R^3 \quad (1)$$

where g = acceleration due to gravity = 9.8 m/s^2 , R is the shell radius, $\Delta\rho$ is the difference in density between the oil drop and the surrounding W2 phase, and γ is the interfacial surface tension.³ Rich Stephens measured the approximate surface tension in this system to be 10 ± 2 dyne/cm.⁴ This equation required that we look at the density mismatch between our O1 solution and our new W2 with the additional CaCl_2 .

Figure 2 shows plots of density versus temperature for pure fluorobenzene, pure water, and 1.5 wt% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ aqueous solution. The fluorobenzene curve is drawn as a straight line through the two known data points at 15 and 30°C.⁵ The curve for water is taken from the CRC.⁶ To approximate the temperature dependence of the dilute CaCl_2 solution, the pure water curve is shifted up to match density at 20°C of 1.0091 g/cc interpolated from the

CRC.⁷ For pure water W2, the density match with O1 appears near 53°C, while the density match for the CaCl_2 W2 is lower near 38°C. Figure 3 shows the estimated max OOR versus temperature of curing, for the two W2 systems, using the density differences in Fig. 2. One sees in Fig. 2 that for pure water W2, the max OOR is near 1 μm at 60°C, but the max OOR for the CaCl_2 W2 is about 3.5, close to the experimentally observed 2–4 μm .

We decreased the curing bath temperature from 60 to 40–45°C when using CaCl_2 , and the shell OOR decreased back below 1 μm (Fig. 1). The temperature for minimum OOR was found to be near 43°C. The increase in temperature from 38 to 43°C is probably explained by the O1 having a slightly higher density than pure fluorobenzene. In later runs, when we replaced the CaCl_2 with NH_4Cl , a similar density match calculation was performed, and the optimum curing bath temperature is at 47.5–48.0°C.

B. STIR RATE

Having corrected the density mismatch by changing the curing temperature, the effect of stir rate in the beaker was studied. We anticipated that the shear developed by the stirrers would deform the spherical shell. Cook³ has estimated the shear effect on max OOR of a simple drop as

$$\text{max OOR} = 4\eta(2\pi * \text{rpm}/60) R^2/\gamma \quad (2)$$

where η is the W2 viscosity = 0.014 poise.⁸

In Fig. 4, the stirring rpm was held constant throughout the curing period, in all the batches. Obviously, there is a shallow minimum in OOR with respect to stir rpm. The straight line is a plot of the Cook equation, with

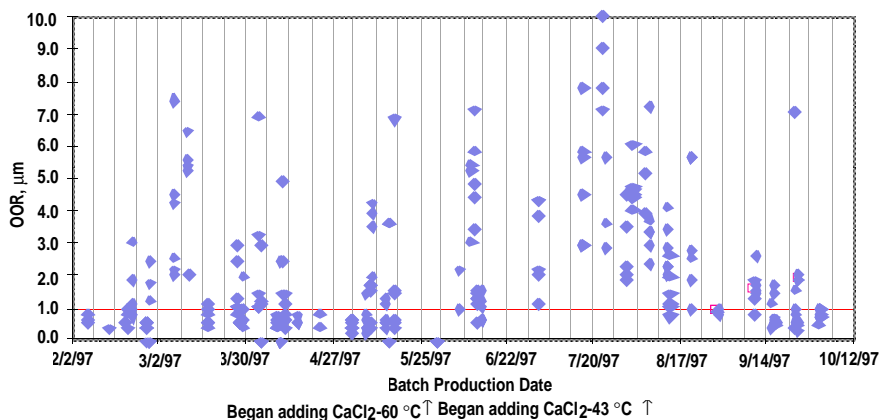


Fig. 1. Omega shell batch OOR as a function of time. Before early May 1997, a 60°C cure and no salt was used. After early May, a 60°C cure was used and CaCl_2 was added. After September 1997, the temperature of the cure was reduced near 43°C, and CaCl_2 was used. Looking at the shell batches with OOR < 1 μm , these two transition dates are quite obvious.

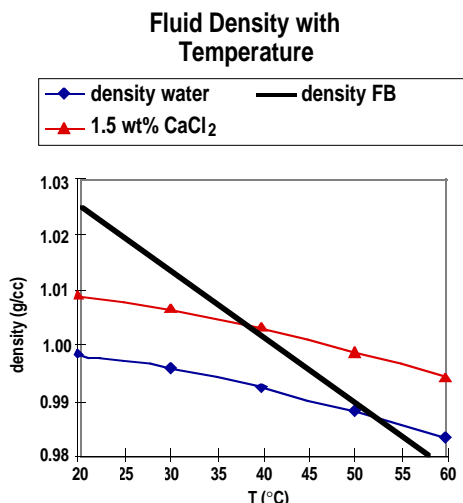


Fig. 2. Plot of solution density vs temperature for fluorobenzene, pure water, and 1.5 wt% CaCl₂*2H₂O. Pure water matches fluorobenzene near 53°C, while the CaCl₂ solution matches fluorobenzene at a lower temperature.

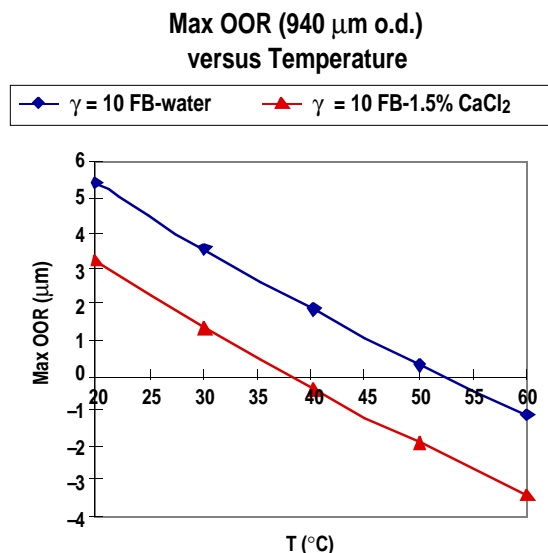


Fig. 3. Using the densities in Fig. 2, the max OOR estimated for the density mismatch as a function of temperature. (γ is estimated to be 10 dyne/cm)

typical values for the shells (the R chosen for the calculation is the maximum radius of the compound drop before any solvent extraction has occurred, 592 μm The calculation uses 0.010 poise for the viscosity). Given the potential uncertainties in the model (a simple drop, not a compound drop) and uncertainties in experimental parameters (shell diameter, surface tension and viscosity), the Cook shear equation seems to describe the high rpm side of the curve, but not the low rpm side.

It is unclear what factor is influencing the dramatic increase in OOR at low rpm. We can speculate that with insufficient stirring, the shells are not tumbling sufficiently. Norimatsu has proposed that tumbling improves the centering of the compound drop, to compensate for any residual density mismatch between W1 and O1.⁹ In our system, there is an inherent mismatch between W1 and O1, since we have chosen to density match O1 with W2. Failure to center W1 within O1 leadsto non-uniform shell walls, a high non-concentricity, which has some correlation to OOR at high non-concentricities. Second, the highest OOR at low stirring occurs with very low PVA concentrations. We have no fundamental understanding of this data.

C. QUANTITY OF FLUOROBENZENE

The third factor which influences the OOR is the total quantity of fluorobenzene present in the beaker. Figure 5(a) shows the data for a single day's run, where the O1/W1 flows [(cc/hour)/cc/hour] were changed after filling two beakers, from 50/50 to 20/20 to 25/20, for

the same PVA W2 flow rate. Thus, the lower flow rates correspond to fewer shells in the beaker, and hence less fluorobenzene. The runs at 50/50 produced the typical shell OOR near 0.5 μm , but the runs with lower flow rates had dramatically poorer OORs. This dramatic change seems to be explained in Fig. 5(b), where the grams of fluorobenzene per beaker are calculated, along with the mark for the literature value for the solubility of fluorobenzene in water at 25°C.⁶

The solubility limit seems to correspond with the change in OOR. It seems reasonable, that if the total quantity of fluorobenzene introduced into the beaker is below the solubility limit, then the fluorobenzene in the drops dissolves into the W2 rapidly, freezing the drops as shells before they can tumble and become spherical. Going above the saturation limit requires evaporation of fluorobenzene from the solution in order to dry the shells. The longer time this evaporation requires apparently permits the shells to become spherical. This effect of fluorobenzene saturation had been noted in making NOVA shells, where the O1 flows are typically lower, where saturating W2 with fluorobenzene before the run improved the NOVA shells' OOR.

III. CONCLUSIONS

The formation of spherical microencapsulated PAMS shells requires control of process variables which govern their sphericity. We have identified three variables (density mismatch, stir rate, and fluorobenzene present in excess of saturation) which must be controlled and

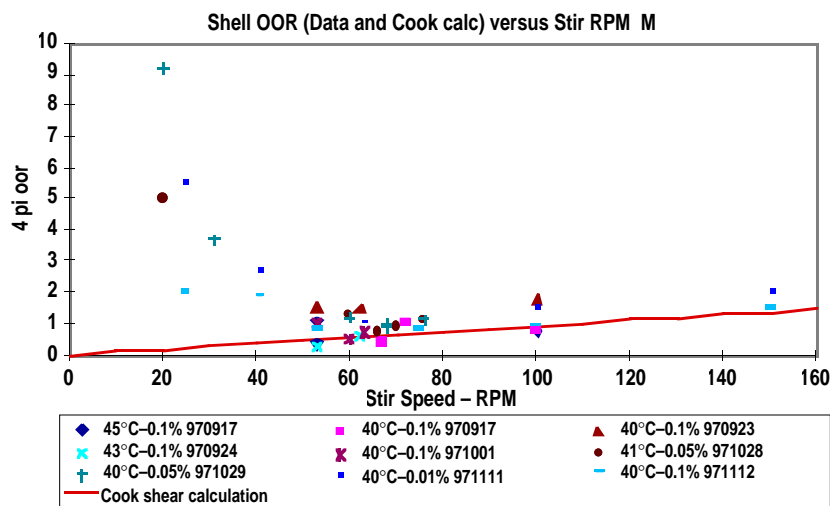


Fig. 4. A plot of experimental OOR versus stir rate in the beaker, and a plot of the Cook shear equation of max OOR versus rpm. (γ is estimated to be 10 dyne/cm, and η of W2 is taken as 0.01 poise.) 0.1% is the PVA concentration (wt%) in W2, unless otherwise noted.

optimized in order to form 1 mm o.d. shells with variation in their diameter around the shell of less than 1 μ m.

ACKNOWLEDGEMENT

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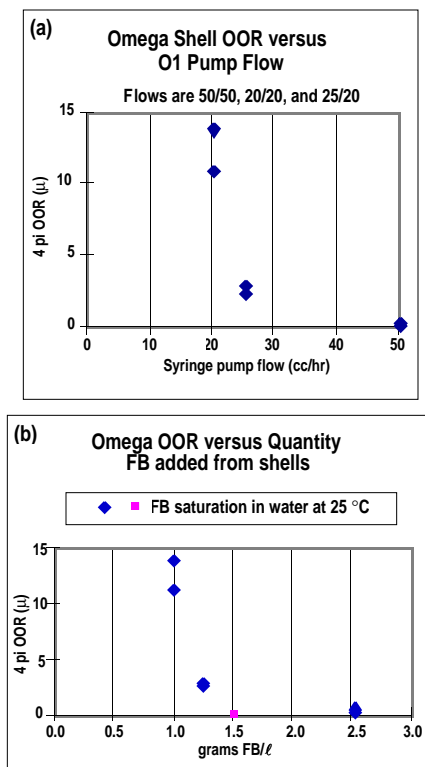


Fig. 5. (a) OOR as a function of the O1 syringe pump flow. (b) OOR as a function of the quantity of fluorobenzene added, with the fluorobenzene saturation level marked at 1.5g/l ■.