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## REMOVAL OF MODE 10 SURFACE RIPPLES IN ICF PAMS SHELLS

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### ABSTRACT

Plastic spherical shells made by microencapsulation show a surface roughness over modes within the range 7–20, generically termed “the mode 10 problem.” The roughness mode number corresponds with theoretical models of Marangoni convection cells formed during the curing of the initial wet shells. The roughness is removed, by appropriate changes in shell processing conditions, changes guided by the understanding of Marangoni convection.

### I. INTRODUCTION

For many years, we have observed surface ripples, or deformations, in “typical” plastic shell mandrels made by microencapsulation, where by typical we mean shells roughly 1 mm in diameter, with a 18  $\mu\text{m}$  thick wall of poly( $\alpha$ -methylstyrene) (PAMS). In measuring the surface smoothness of the shell on a spheremapper,<sup>1</sup> we noted surface bumps and valleys of order 0.1–1  $\mu\text{m}$  high, with a mode number of 7–9. When we began making 2 mm mandrels, we observed the same bumpiness, but with mode numbers slightly higher. The origin of these specific long range and reproducible deformations puzzled us.

We propose that the bumps are produced by Marangoni convection cells induced by removal of solvent in the shell curing. The deformations in the final dry shell reflect the convection cells and transport of polymer in the initial wet shell. By changing the process parameters in ways consistent with the elimination of these Marangoni convection cells, we have eliminated the deformations. The amplitude in the mode 10 region has been dramatically reduced. Theoretical calculations of the mode structure are shown to be consistent with the observed data.<sup>2</sup>

Marangoni convection has been studied both experimentally and theoretically in flat films for more than forty years.<sup>3–6</sup> Marangoni convection generally refers to

transfer of heat caused by surface tension gradients parallel to the film surface, correlated typically with macroscopic temperature gradients perpendicular to the film surface. The surface tension gradients are caused by temperature gradients with scale length on the order of the film thickness along the surface. However, Marangoni convection is also known to occur in drying films (transfer of solvent),<sup>6</sup> where the surface tension fluctuations are correlated with concentration gradients. In a spherical geometry, the analogous Rayleigh convection has been studied heavily. Rayleigh convection is caused by density gradients, induced by temperature or concentration gradients. To date, Marangoni convection in spherical geometry has not been the subject of much experimental investigation.<sup>7,8</sup>

### II. EXPERIMENTAL

#### A. Shell Production

For the sake of this paper, two different types of shells are considered: 1 mm OD shells (940  $\mu\text{m}$  OD Omega shells) and 2 mm OD shells (NIF shells). The plastic shells are produced via a dual orifice microencapsulation method,<sup>9–12</sup> using PAMS (Poly- $\alpha$ -methylstyrene) (SPP, 400 K MW, polydispersity = 1.04) dissolved in fluorobenzene (FB-Aldrich). This polymer solution is called “the oil phase” O1). There is a central drop of pure deionized water (W1). The compound drop is suspended in an aqueous solution (W2) of either 0.3 wt% PVA (polyvinylalcohol - 98% hydrolysed, 25 K MW, Polysciences) for 1 mm shells, or 0.05 wt% PAA (polyacrylic acid, 1 M MW, Polysciences). These shells are made in somewhat different processes. The total range of differences will not be summarized here, only those process variables which directly pertain to the presence and/or absence of Marangoni convection. A summary of the pertinent comparisons is found in Table I.

It should be noted, that the choice of fluid densities is such, that the shell sees a near zero gravity (milli-gravity)

TABLE I

Parameter	OMEGA		NIF	
	Convection	No Convection	Convection	No Convection
OD (wet)	1184 $\mu$	1184 $\mu$	2521 $\mu$	2197 $\mu$
OD (dry)	940 $\mu$	940 $\mu$	2056 $\mu$	2080 $\mu$
Wet wall Thickness	122 $\mu$	122 $\mu$	260 $\mu$	65 $\mu$
PAMS-O1 (wt%)	11	8.0	10	18
Dry wall Thickness	18 $\mu$	13 $\mu$	40 $\mu$	14 $\mu$
Temperature	48°C	48°C	25°C	25°C
Stirring Method	Mechanical stir in open beakers		Stir in rotovaps, not stirrers	
Time of Curing	3–6 hours	3–6 hours	4 days	4 days
Use of Bubbler	None	None	FB bubbler	FB bubbler
Mode Observed	7–9	None	9	None
Mode Estimated by $\pi OD/(4 \times \text{wet wall})$	7.6		7.6	

condition. Fluorobenzene is chosen as the solvent, since its density is 1.024 at 20°C, and is very similar to water near 45°C. Likewise, the temperature for curing is chosen, such that the composite shell density changes minimally throughout the curing, and stays density matched with the W2. These density matched conditions minimizes any density-driven Rayleigh convection conditions.

### B. Spheremapper Measurement

To measure the shell surface on the spheremapper, a shell is held on a vacuum chuck, and the chuck is rotated 360° under the AFM tip. A scan is gathered “at the equator,” and then two scans  $\pm 10 \mu\text{m}$  above and below the equator are similarly gathered. The shell is then rotated 90°, and another three scans about an orthogonal axis are obtained. The shell is then rotated 90°, orthogonal to the

other two axes, and a third set of three scans are obtained. The nine scans are each Fourier-transformed, squared, and then averaged to obtain a curve of the power spectrum versus mode number for the shell.<sup>1</sup>

Figure 1(a) shows the power spectrum of the nine scans, collected from a 1 mm shell. The upper curve shows a bump near mode 8 (over a range of mode 7–9) on the scan. This bump is repeatedly observed in 1 mm OD shells, made with the conditions listed above.

### III. REMOVAL OF THE MODE 10 DEFECT

The onset of Marangoni convection occurs when the Marangoni number  $M$ , exceeds a critical value  $M_c$ , for

$$M = (d\gamma/dC)(\Delta C) L / (\eta D) \quad (1)$$

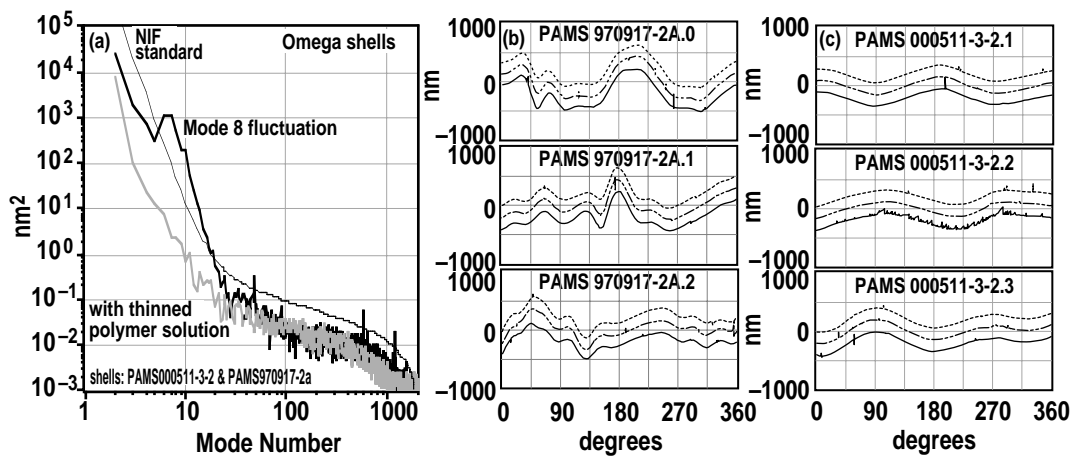


Fig. 1. (a) Shows the power spectra of a 1 mm shell with a mode 10 peak (upper curve) and a shell without a mode 10 peak (lowest curve). The middle smooth curve is the specified “NIF spectrum.” (b) Shows the surface bumpiness of the shell with mode 10. (c) Shows the surface bumpiness of a shell without mode 10.

in spherical geometry, where:  $(d\gamma/dC)$  is the change of surface tension with fluorobenzene concentration along the surface;  $(\Delta C)$  is the fluorobenzene concentration gradient perpendicular to the surface;  $L$  is the thickness of the polymer solution wall;  $\eta$  is the polymer solution viscosity; and  $D$  is the diffusivity of the fluorobenzene in the polymer solution. For flat films, the value of  $M_c \approx 80$ . Typically, the value can vary depending on boundary conditions, such as whether the layer is insulating or conducting, whether the film has a fixed or distortable surface, etc. This value of 80 is to be considered representative for flat films.

With the hypothesis of Marangoni convection being the source of the mode 10 defect in these two distinct types of shells, we sought to reduce the Marangoni number below the critical value  $M_c$ . Many of the experimental values which comprise this number are unknowns, so the actual value of the Marangoni number at the beginning of curing is unknown. While we have few quantitative values, the equation does provide a direction to guide how to change the process variables. For instance, as curing proceeds, and fluorobenzene is lost, the Marangoni number would probably decrease, and at some point would fall below the  $M_c$ . As the shell cures, the thickness  $L$  of the O1 layer grows thinner, and the viscosity increases as the polymer concentration increases, terms which should dominate the changes in  $M$  as the shell cures.

In seeking to decrease  $M$ , three terms  $(\Delta C, L, \eta)$  can be directly correlated to process condition. One would seek to decrease the value of the first two terms and increase the value of viscosity.  $\Delta C$  can be reduced by slowing the curing rate  $dC/dt$ . From Fick's Law at steady-state, with a diffusion constant  $D$  and layer thickness  $L$ ,

$$\Delta C = (\text{shell surface area}/D)(dC/dt) = (dC/dL)L = k(C_s - C^*) \quad (2)$$

where  $k$  is a mass transfer coefficient for fluorobenzene coming out of the W2 and into the vapor above the W2. This argument presumes that the shells' fluorobenzene is in near equilibrium with the fluorobenzene concentration in the W2, so that the rate of loss of fluorobenzene from the shells equals the rate of loss of fluorobenzene from the W2.  $C_s$  is the vapor pressure of fluorobenzene directly at the W2 surface, and  $C^*$  is the vapor pressure of fluorobenzene in the vapor. In our initial work for 2 mm shells, we had pumped air above the W2 to drive out fluorobenzene vapor, thus maintaining the vapor concentration of fluorobenzene  $C^*$  near zero. The curing rate  $dC/dt$  was first altered by adding a bubbler with 60 cc of fluorobenzene (FB bubbler in Table I). Pumping air

thru the fluorobenzene bubbler would lead to a larger value of the fluorobenzene vapor pressure  $C^*$  in the vapor, so  $C^*$  would be larger and  $(C_s - C^*)$  would be smaller. However, this change in process variable alone is not sufficient to eliminate mode 10.

To decrease the Marangoni number, viscosity can be increased by increasing the polymer concentration, or by increasing the PAMS molecular weight. Changes in O1 concentration also effects the final dry shell wall thickness, which must be kept in mind in making these shells. In the 1 mm and 2 mm examples given in this paper, viscosity and O1 thickness are changed in different ways to remove mode 10.

Table I shows an example of 2 mm NIF shells, and Fig. 2 shows the dramatic change in mode 10. In this example, the O1 concentration was increased, and the thickness of the O1 was decreased, in order to decrease  $M$ . The viscosity of the O1 changes from about 36 centipoise (10 wt%) to 277 centipoise (18 wt%), and the initial wet shell O1 thickness changes from 260 to 65  $\mu\text{m}$ . Thus,  $L/\eta$  decreases 31-fold. If all other factors remained constant, then the Marangoni number has been reduced 31-fold, and apparently  $M$  has been reduced below the critical value.

Table I also shows an alternate way to eliminate mode 10 in Omega shells, by a decrease in O1 viscosity (see Fig. 1). This decrease in O1 viscosity seems counterintuitive to the Marangoni convection argument which would call for an increase, but is actually consistent with the argument. To make a thinner dry wall for Omega shells, we chose to decrease the O1 concentration, which decreases the viscosity, while keeping the same initial wall thickness  $L$ . For the discussion below, consider the time dependence of  $M$  as the shell proceeds to cure by loss of fluorobenzene. To clarify the following language,  $M_{11\%}$  refers to the Marangoni value of a shell made initially at 11%, and  $M_{8\%}$  refers to the Marangoni value of a shell made at 8% O1. The term  $M_{8\%}(11\%)$  then means the value of the Marangoni number of a shell initially made at 8%, but which is now at 11%. Other terms used will follow this pattern. Figure 3 corresponds with the following discussion.

In decreasing the initial O1 concentration from 11 wt% to 8 wt%, the initial viscosity  $\eta$  of the O1 would be smaller, thus increasing  $M$  [all other parameters presumed the same,  $M_{8\%}(8\%) > M_{11\%}(11\%)$ ]. However, as the 8% shell cures, at some point the O1 is 11%, and at this point the value of  $L$  is smaller than for the shell made from 11% O1. Thus,  $M_{11\%}(11\%) > M_{8\%}(11\%)$ . This 8% shell, now at 11% O1, is now closer to  $M_c$  (if it has not already gone below  $M_c$ ). There are two possible cases to consider. In

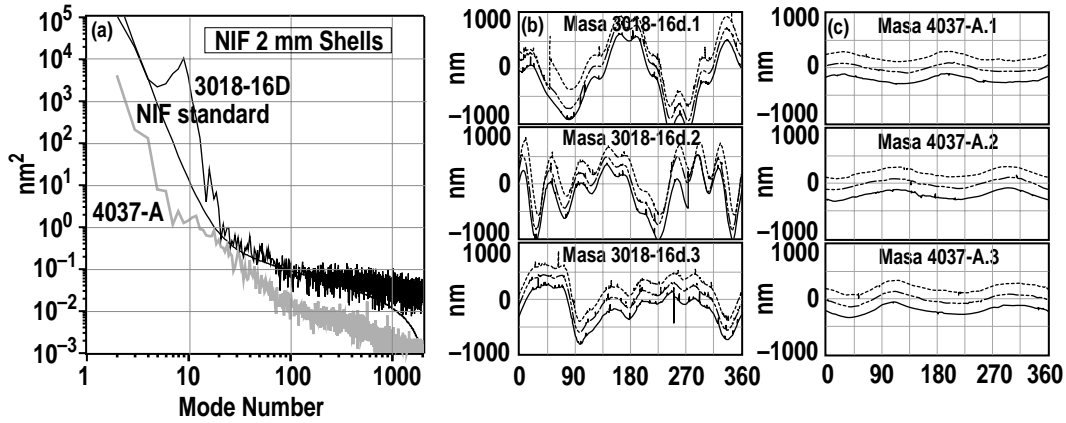


Fig. 2. (a) Shows the much higher power peak near mode 10, compared to a shell without mode 10 peak. (b) Shows the mode 10 bumpiness on the shell surface. (c) Shows the lack of mode 10 bumpiness.

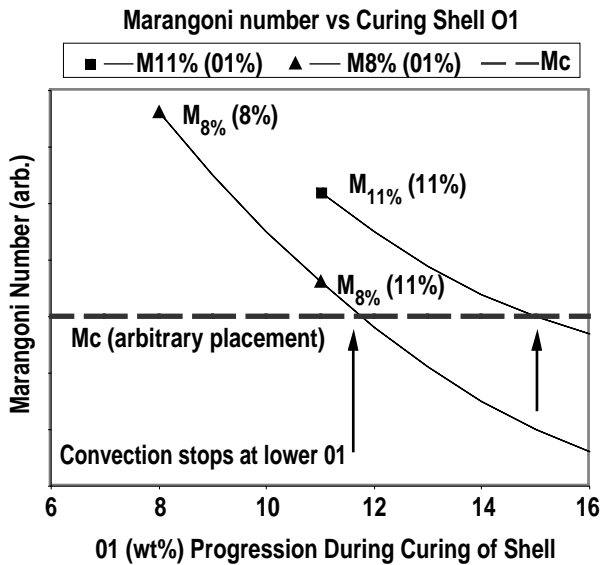


Fig. 3. Progression of shell marangoni number as shell cures.

the first case, for the 8% shells, at the 11% concentration, convection still exists. ( $M_{11\%}(11\%) > M_{8\%}(11\%) > M_c$ ; see Fig. 3. However, since the 8% shell is closer to  $M_c$ , convection will shut off shortly, at a lower O1 wt% (~12%), than would the 11% shell (~15%). Any ripples due to convection cells which had formed at 8%, now have a sufficiently low viscosity fluid that the ripples can relax back into the surface. The mode 10 ripples will subside into a smooth surface. The convection shut off occurs at a lower O1 viscosity.

As an alternate way to understand this  $M_{8\%}$  curing curve, we could intuitively reduce the Marangoni number by using the same 11% O1, but make the wet O1 wall thinner. This condition would be exemplified by the point  $M_{8(11\%)}$ . The curing curve (O1 concentration versus wall

thickness) would be the same, from this point in time forward, as a shell which started earlier in time as  $M_{8\%}(8\%)$  with a thicker wall, and had now arrived at  $M_{8\%}(11\%)$  during the curing. By starting with the same initial wall thickness  $L$ , but with 8% O1 rather than 11% O1, we have arrived at the same point, closer to  $M_c$  and closer to the shut off of Marangoni convection, as if we had made the O1 wall thinner at the beginning.

The classical Marangoni arguments are made for a static quasi-equilibrium fluid system, where the fluid remains at constant thickness and constant viscosity. By considering this mechanism of surface relaxation upon cessation of convection, this counterintuitive process change of reducing the O1 viscosity is shown to still be consistent with Marangoni arguments. The convection cells are formed by Marangoni convection at early times, yet they also shut off at earlier times.

#### IV. OBSERVED MARANGONI MODE

One final point to be raised is, in a given wet shell, what mode number does one expect to see? In flat films, the mode observed corresponds to twice the thickness of the liquid layer. Our shell's liquid layer O1 is changing during the curing, so which mode number will be observed is open to question. However, the mode number observed seems to correspond with the initial wet compound drop O1 thickness. In using the initial O1 thickness, one finds a good correlation to the experimental mode observed with 4 times the initial O1 thickness as the scale length of the mode observed.<sup>2</sup> The initial O1 thickness is where the viscosity is lowest, and the thickness is highest, so the value of the Marangoni number is highest. If the convection cells form, they are most likely to do so near the initial conditions. It appears that the initial mode number persists during the O1 curing.

## V. SUMMARY

The mode 10 defect has been eliminated in PAMS mandrels by suitable changes in process parameters. The process changes have been guided by the understanding that Marangoni convection cells form during the curing.

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