GA–A24483

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SEPTEMBER 2003

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This is a preprint of a paper presented at the 15th Target Fabricartion Specialists Meeting, Gleneden Beach, Oregon, June 1–5, 2003 and to be published in *Fusion Science and Technology.*

Work supported by
the U.S. Department of Energy
under Contract Nos. DE-AC03-01SF22260
and W-7405-ENG-48

GENERAL ATOMICS PROJECT 30095
SEPTEMBER 2003

PROGRESS IN 2 mm GLOW DISCHARGE POLYMER MANDREL DEVELOPMENT FOR NIF

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All planned National Ignition Facility (NIF) capsule targets except machined beryllium require a glow discharge polymer (GDP) mandrel upon which the ablator is applied. This mandrel, ~ 2 mm in diameter, must at least meet if not exceed the symmetry and surface finish requirements of the final capsule. Such mandrels are currently produced by the three-step depolymerizable mandrel technique.[1] The quality of the final mandrel depends upon precise optimization and execution of each of the three steps. We had shown previously that fabrication of a mandrel which met the symmetry and surface finish requirements was feasible using this technique. In this paper we will discuss recent progress towards converting this process into a high yield, production scale process.

I. INTRODUCTION

Several of the fabrication schemes for production of indirect drive NIF capsules require a CH mandrel, ~ 2 mm diameter, preferably thermally stable, as a substrate for deposition of the ablator material. The various ablator materials include beryllium,[2] polyimide[3] and plasma polymer.[4] The required symmetry and surface finish specification of the final ablator surface, obtained by spheremapping[5] shells using atomic force microscopy (AFM), was set a number of years ago in terms of the allowed power in the various modes in the spherical harmonic decomposition of the shell surface and has been referred to as the NIF standard. The symmetry and surface finish of the ablator is greatly influenced by that of the mandrel. In fact, for all the ablators proposed, the symmetry of the final shell cannot be any better than the starting mandrel for almost all spherical harmonic modes. Therefore, it is crucial that the polymer mandrels have the required properties. GDP has been chosen as the polymer of choice due to its thermal stability, which is particularly important for the beryllium and polyimide processes where the mandrels can be subjected to high temperatures during deposition or processing. Such mandrels are produced using the three-step depolymerizable mandrel technique. In the first step of this process, a thin-walled poly(α-methylstyrene) (PAMS) shell is produced using microencapsulation. This shell is then overcoated with 10 to 15 μm of GDP. The final step is pyrolysis at 300 °C to depolymerize the PAMS to gas phase monomer that diffuses away through the thermally stable GDP shell. This technique is currently used for fabrication of nearly all shells used in the various ICF experiments. We had demonstrated previously that fabrication of such a mandrel which met the NIF standard was feasible by this technique.[6] However, the reproducibility of this process in yielding NIF quality GDP mandrels had not been demonstrated. In fact, the reproducibility had been found to be in general rather poor (<10%). High reproducibility is essential for this technique to be of practical use for NIF target fabrication. This paper presents the steps taken to investigate and attain reproducible NIF quality GDP mandrel (thickness limited to ~ 10–15 μm) fabrication.

II. EXPERIMENT

Each one of the three steps involved for GDP mandrel fabrication was examined in detail for reproducibility. The experiments and results obtained for each steps are discussed in the sections below. The PAMS fabrication details are limited only to that relevant for 2 mm PAMS shell fabrication. Characterization was performed by optical microscopy and interferometry, but the main characterization tool was spheremapping. Three AFM traces were taken about three orthogonal axes on each shell. Enough shells (typically ~ 10) from each of the selected batches were spheremapped to obtain relevant statistics. It should be noted that in the spheremap power spectra shown, no traces have been eliminated as is customary to do if a large isolated feature is encountered in a trace.

III. FABRICATION OF PAMS SHELLS

The baseline 2 mm PAMS microencapsulation process was developed by Takagi, et. al.[6] In what follows

we shall refer to this baseline process a number of times. It involves the use of high molecular weight (HMW) poly(acrylic acid) (PAA) as the stripping fluid and then washing the shells after several days (typically 48 h) of curing with 88% hydrolyzed, 2.5×10^4 molecular weight (M_W) poly(vinyl alcohol) (PVA). The details of this process are presented in Ref. 6. Briefly, the important findings are as follows. The use of PAA as the stripping fluid results in highly spherical and concentric PAMS shells but also can lead to excessive high frequency surface roughness after GDP coating. The rough GDP surface was found to be due to left over PAA gel residue on the GDP surface. However, implementing a PVA washing step after the proper amount of curing was found to retain the sphericity of the PAMS shells while removing the PAA from the surface of the shells and avoiding the rough GDP surface. Using this baseline PAMS fabrication technique and the subsequent GDP and pyrolysis steps we had shown the feasibility of producing a NIF quality GDP mandrel. However, the reproducibility of this process and variations to it had not been fully investigated. The previous effort in developing the baseline process had concentrated on freely exploring the parameter space of the process without focusing on the reproducibility of a given successful variation. In addition, the baseline process itself exhibited poor reproducibility, with only about one out of over ten batches being NIF quality. This yield was too low for a practical production effort. In this study, we examined only several variations to this baseline PAMS fabrication process and concentrated on examining the reproducibility of each variation to the baseline process. We typically fabricated over twenty batches using each one of the processes described below, keeping the fabrication parameters constant for each variation.

The first variation involved adding low molecular weight (LWM) PAA ($M_W\sim 5\times0^3$) early in the curing stage to replace the initial HMW PAA ($M_W \sim 1$ M) around the PAMS shells. The excessive high mode roughness observed on the shells made using the baseline process after coating with GDP was thought to be due to gelation of the HMW PAA on the PAMS surface. It was hoped that the LMW PAA, which does not gel due to its low molecular weight, would replace the HMW PAA around the PAMS shells and still retain the sphericity. The PVA washing step was kept the same as the baseline process. However, while the shells made this way still had low out-of-roundness (mode 2), the high frequency roughness was still present and in addition some middle frequency roughness also appeared. Therefore, this technique was not pursued further due to the poor quality of the PAMS shells.

The other variation involved washing using various types of PVA. The motivation was that PVA of different molecular weight or hydrolysis level may be more effective in replacing the PAA on the PAMS shells during the washing step and lead to consistently better surface finish after GDP coating. The different types of PVA examined were: 2.5×10^4 M_W, 98% hydrolysis; and 1.25×0^5 M_W, 88% hydrolysis. In all of these, the initial PAA solution was exchanged with 2–3 wt% of the chosen PVA solution as in the baseline technique. We found that both of these techniques exhibited better reproducibility than the baseline technique both within a batch and from batch to batch. As an example of reproducibility within a batch, Fig. 1 shows the AFM power spectrum of a random sampling of ten shells in the same batch that was made by the first variation, that is, replacing PAA after 48 h, with 2 wt% 2.5×10^4 PVA (98% hydrolysis), before finishing the curing. Almost all power spectra were below the NIF standard power specification curve, showing excellent reproducibility within a batch. Figure 2 illustrates the reproducibility from batch to batch of twenty runs using the second variation, using 1.25×10^5 M_W, 88% hydrolysis PVA for the exchange. 40%–50% of the batches meet the NIF standard. The reproducibility within a batch for this process was similar to the first. This level of reproducibility, while not perfect, was sufficiently high enough for the production levels required for NIF mandrels and is actually similar to those of 1 mm shells. Currently, we have adopted the 1.25×10^5 M_W, 88% hydrolysis variation as the new baseline for 2 mm PAMS fabrication, although the reproducibility of the two techniques are rather similar. While the PAMS shell power spectra were very promising, we needed to verify that no residual high mode surface roughness would develop after the GDP coating as had been observed previously.

IV. GDP COATINGS

Having obtained sufficient reproducibility in fabrication of PAMS shells, we investigated the yield of

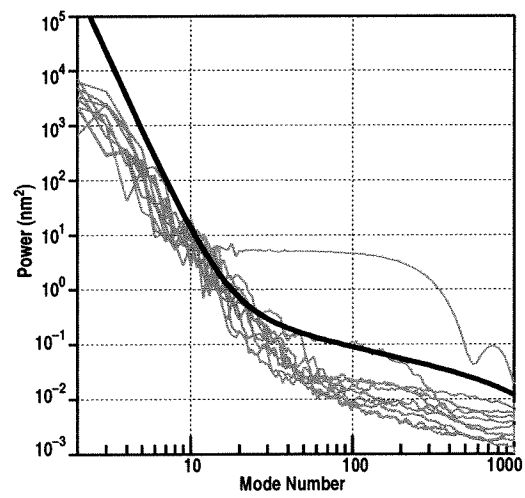

Fig. 1. AFM power spectra of a random sample of ten shells from batch made by exchanging PAA with 98% hydrolyzed, 25×10^5 M_W PVA. As can be seen most shells meet the NIF curve (darker bold line) demonstrating reproducibility of the process within a batch.

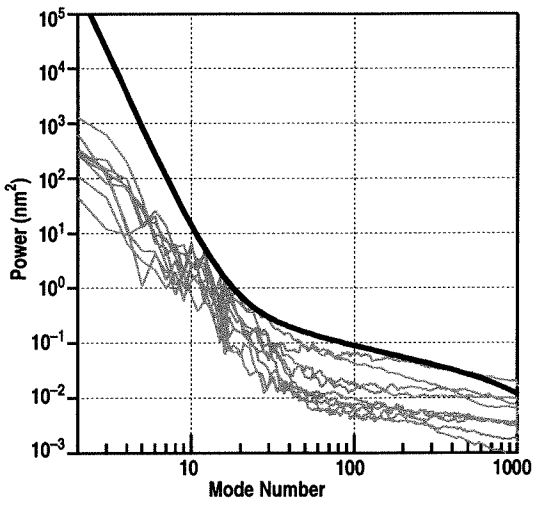

Fig.. 2. AFM power spectra of shells from 20 different batches made by exchanging PAA with 88% hydrolyzed, 1.25×10^5 M_W PVA. 40% of these batches were NIF quality. The reproducibility of power spectra within a given NIF quality batch made using this technique was similar to what is shown in Fig. 1.

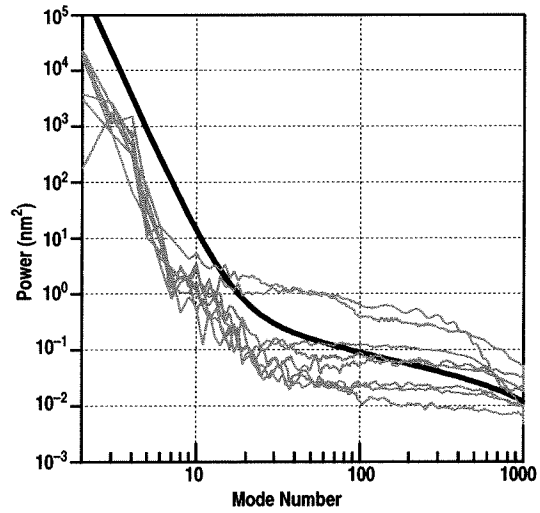

Fig. 3. AFM power spectra of GDP (~ 12 μm) coated PAMS shells. A large fraction of these shells have spectra at or below the NIF curve. Therefore, the GDP process does not lead to degradation of shell quality.

the GDP step. We performed tens of GDP runs depositing 12–15 μm of GDP on PAMS shells produced with the new variations. The processing procedure was changed to ensure minimal amount of exposure to non-clean environments as possible. The vials containing the PAMS shells were kept either in class 100 cleanroom or in a clean hood which was placed over the coater. Shells were transferred to the coating pan directly without any handling and the coating pan was loaded directly in the coater without removal from the clean hood. Only ~10 shells were coated at a time and the shells were bounced as gently as possible to avoid agitation induced dome formation[7] during coating. A typical result obtained using these procedures is shown in Fig. 3. As can be seen many of the shells (>70%) had power spectra that were below the NIF curve. This showed that the coating step leads to minimal degradation of the quality of the shells. In addition, it confirmed that the PVA exchange process in PAMS fabrication did in fact remove the PAA residue to a sufficient extent so that no excessive overall high mode roughness was developed. An occasional large dome (~ 1 μm or more tall, tens of microns wide) was encountered on a few GDP coated shells. This was the main source of power seen above the NIF curve in the spectra of GDP shells. The origin of the domes is presumably defects (possibly small debris) on the original PAMS mandrels. Given the minimal and clean handling of the PAMS shells, the debris most likely was on the PAMS shells immediately after fabrication, possibly polymeric debris generated during curing. Despite the presence of these occasional large domes, these results were very encouraging as this was the first time since the early demonstration run[6] that GDP coated shells this far below the NIF curve were produced. Of course, these shells still contained the PAMS mandrel, but if the pyrolysis was performed successfully then a large percentage of pyrolyzed GDP shells from these runs should have met the NIF curve.

V. PYROLYSIS

With the encouraging results obtained from coating the newly fabricated batches of PAMS shells we proceeded to the final step of pyrolyzing the mandrel out of the shell. GDP coated PAMS shells from the new superior batches were used. Surprisingly, the sphericity of most of the pyrolyzed shells was so poor that they could not even be spheremapped using our recently upgraded spheremapper which has an expanded 6 μm range. Also, a few of the shells had exploded during pyrolysis. Several subsequent batches could be spheremapped but the power spectra had large low and middle mode power as shown in Fig. 4. These results were not expected as a wealth of prior pyrolysis data[8] suggested that sphericity of the GDP shells was similar to those of the PAMS shells. While these results using the newer PAMS shells were rather disturbing, they did point us to a possible mechanism which would eventually aid in obtaining higher reproducibility for the process.

The mechanism suspected of causing such degradation was the residual solvents left in the newly fabricated PAMS shells. Presence of substantial amounts of such solvents was inferred two different ways. First, mass spectrometer analysis of PAMS shells heated to ~ 150°C showed substantial amounts of 2-propanol (used in drying of shells) and detectable amounts of fluorobenzene (used in fabricating the shells) were present in the newly fabricated shells. Secondly, heating of these newly made batches of PAMS shells without any GDP overcoating while observing them under a microscope revealed that

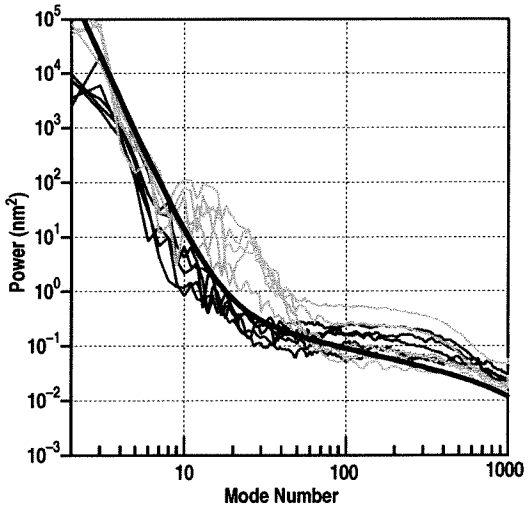

Fig. 4. AFM power spectra of GDP shells after pyrolysis (gray traces – those above the NIF curve in low and middle modes) and those of the GDP coated PAMS shells prior to pyrolysis (darker traces; those at or below the NIF curve). The pyrolysis step had resulted in major degradation of shells due to residual solvent content of the PAMS shells.

they expanded significantly at temperatures (~150–160°C) far below the onset of depolymerization (> 220°C) and also below the glass transition (T_g) of PAMS which is ~ 180°C. This is shown in Fig. 5. This indicated that there were potentially significant amounts of solvent leftover inside the shells as well as possibly in the shell wall. The residual solvents lower the PAMS T_g and the pressure build up inside the shells resulted in the observed expansion. This also could lead to early pressure build up inside the GDP coated PAMS shells at ~150–160°C. At these relatively lower temperatures the GDP is less permeable and the pressure build up can result in deformation of the GDP shell.

Pre-baking of PAMS shells to remove the residual solvents was a natural solution. This needed to be performed at a temperature below the glass transition temperature of the PAMS shells to avoid deforming the PAMS. Pre-baking was done at three different temperatures. To expedite the pre-baking process, initially it was performed over several days at temperatures, ~ 140°C, just below where PAMS shells were observed to soften. While this indeed removed most of the residual solvents, it also caused the 2 mm PAMS shells to soften over time, even at ~ 140°C, and stick to each other, rendering them useless. The pre-baking temperature was then reduced to 120°C. While this avoided any obvious shell-to-shell sticking problem, the PAMS shells developed excessive middle mode power. The encouraging result with these shells was that the final pyrolyzed GDP shells were not severely deformed and had power spectra similar to the GDP coated PAMS shells. The next iteration involved pre-baking shells in individual compartments at ~ 120°C to avoid any subtle

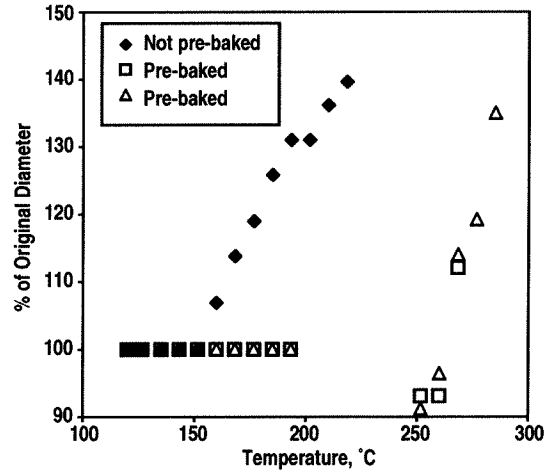

Fig. 5. Diameter expansion of PAMS shells which had been made shortly before this experiment as a function of temperature. No significant expansion should occur at temperatures below ~ 220°C. However, non-pre-baked shells (dark diamonds) begin to expand starting at as low as ~ 150°C. Pre-baked shells (open triangles and squares) do not change size until the expected temperature.

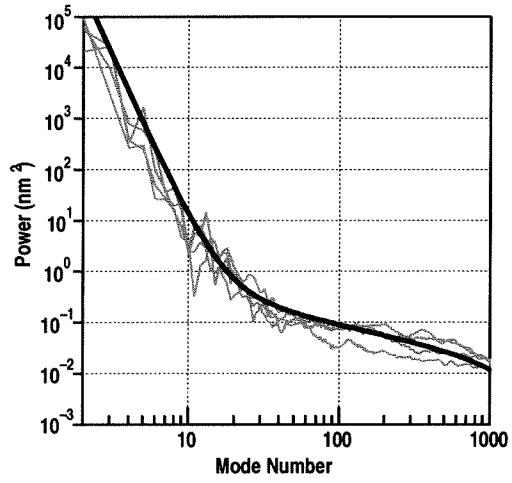

Fig. 6. AFM power spectra of a batch of fully pyrolyzed GDP shells from GDP coated PAMS shells which were pre-baked at ~ 120°C prior to coating. Most shells are at or below the NIF curve as desired. This was typical of shells with such a pre-treatment.

sticking problem during pre-baking. This greatly improved the spectra of final GDP shells as a typical set of power spectra shows in Fig. 6. The results were consistent for several batches.

Although pre-baking at 120°C in individual holders appeared very promising, due to the additional handling involved, often these shells picked up more debris in the pre-baking step. In fact, some GDP batches made using PAMS shells pre-baked at 120°C exhibited higher density of domes, most probably caused by debris introduced in

handling. To avoid any handling prior to coating while reducing the residual solvent content of shells we decided to allow some of the shells to be "pre-baked" at room temperature. This would be the gentlest pre-baking procedure, but one that would take the longest time. The power spectra obtained when GDP coated shells pre-baked at room temperature were pyrolyzed is shown in Fig. 7(a) and 7(b). The pyrolyzed final GDP shells were mostly at or below the NIF curve. This appeared to be a consistent result for this type of pre-baking and is one that we have adopted currently. The yield so far is about the same as what we have obtained in the GDP process (~70%), with the main cause of a shell not meeting the NIF curve being an isolated high frequency feature. The major problem with such a treatment is the length of time involved. The PAMS shells used for these runs were left at room temperature for about two months. However, this does not impose a prohibitively long processing time given that PAMS batches are made continually and this treatment can be considered as a longer than usual drying step.

One other subtle problem with the pyrolysis that is worth mentioning is that our results indicated that if the pyrolysis was performed at too low a temperature (or equivalently, too short a time), some of the PAMS mandrel remained in the GDP shell and apparently led to wrinkling of the shell upon re-solidification. An extreme example of this is shown in Fig. 8(a) and 8(b), where a temperature of only 295°C was used for pyrolysis and pools of PAMS could be seen inside the shell by interferometry [Fig. 8(a)] as well as transmission microscopy. The spheremapper traces showed a severely wrinkled shell [Fig. 8(b)]. Therefore, too low a pyrolysis temperature can lead to severe degradation of the GDP shells and 300°C was used for all pyrolysis work described in this paper.

VII. CONCLUSIONS

We have carried out an extensive study of the reproducibility of GDP NIF mandrel, ~ 2 mm diameter, 10–15 μm thick GDP shell, fabrication. We have developed procedures that lead to a high yield process for fabrication of such shells using the depolymerizable mandrel technique. Modifications to the PAMS shells fabrication has increased the yield of good batches from ~ 10% to ~ 40%–50%. Extensive spheremapping of shells within "NIF quality" batches indicate that > 70% of the shells meet the NIF curve. This high yield of NIF quality shells is preserved through the GDP and pyrolysis steps. Minimal and clean handling of shells is required for the GDP coating step. Residual solvents in the PAMS shells can degrade GDP shell quality during pyrolysis. Removal of these residual solvents from the PAMS shells before GDP coating is essential in obtaining fully pyrolyzed NIF quality GDP shells. Incomplete pyrolysis of PAMS can also degrade the GDP shells possibly due to resolidification of the PAMS inside the GDP.

ACKNOWLEGMENT

Work supported by U.S. Department of Energy under Grant number DE-AC03-95SF20732.

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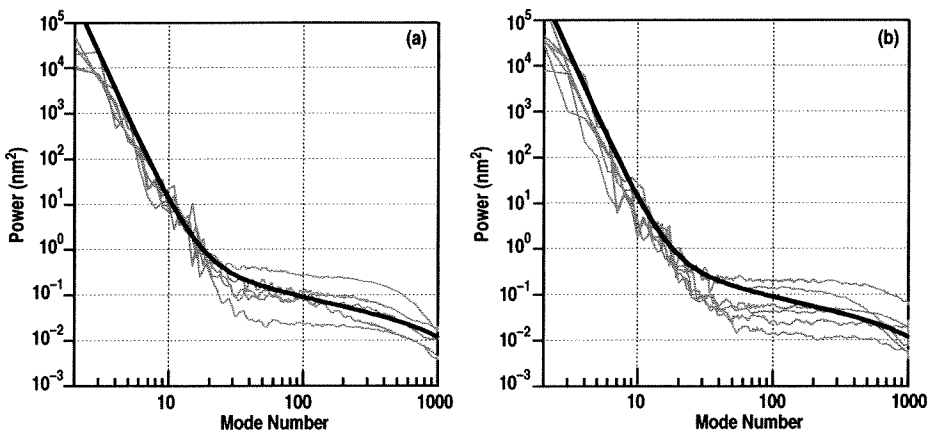

Fig. 7. (a&b) AFM power spectra of two different batches of fully pyrolyzed GDP shells. These shells were made using room temperature pre-baked PAMS shells. Again most shells are at or below the NIF curve.

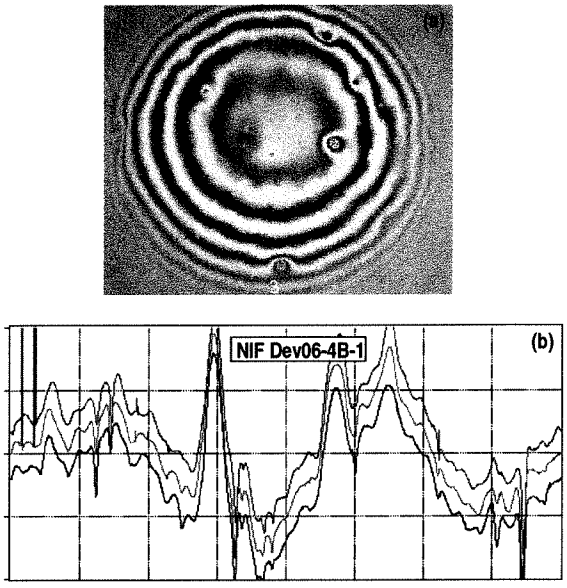

Fig. 8. (a) Interferometric image of a GDP shell obtained by pyrolysis at only 295°C as opposed to the baseline temperature of 300°C. The deviations in the fringes are due to pools of material, presumably PAMS left behind due to insufficient pyrolysis. The image shown is ~ 700 μm wide. (b) The AFM spheremap traces of the same shell showing severe degradation of the surface of the shell due to the left over PAMS. The GDP coated PAMS shell prior to pyrolysis had a smooth surface.

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