

# Challenges in Laser Sintering of Melt-Processable Thermoset Imide Resin

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## ABSTRACT

Polymer Laser Sintering (LS) is an additive manufacturing technique that builds 3D models layer by layer using a laser to selectively melt cross sections in powdered polymeric materials, following sequential slices of the CAD model. LS generally uses thermoplastic polymeric powders, such as polyamides (i.e. Nylon), and the resultant 3D objects are often weaker in their strength compared to traditionally processed materials, due to the lack of polymer inter-chain connection in the z-direction. The objective of this project is to investigate the possibility of printing a melt-processable RTM370 imide resin powder terminated with reactive phenylethynyl groups by LS, followed by a postcure in order to promote additional crosslinking to achieve higher temperature (250-300 °C) capability. A preliminary study to build tensile specimens by LS and the corresponding DSC and rheology study of RTM370 during LS process is presented.

## 1. INTRODUCTION

The two major techniques applied to the 3D printing of solid state polymers by additive manufacturing are: 1) Fused Deposition Modeling (FDM) which melts a polymer filament and deposits successive layers of polymer to build a 3D component. 2) Polymer Laser Sintering (LS) which builds 3D models by using a laser to selectively melt cross section in powdered polymeric materials layer by layer, following the slice of each CAD scan. These two types of 3D printing use thermoplastic filaments or powders, respectively; and the resultant 3D objects are often weak in their strength compared to traditionally processed materials, due to the lack of polymer inter-chain connection in the z-direction. Previous effort has demonstrated the feasibility of printing novel melt-processable thermoplastic polyimide filaments (Co-PI-265,  $T_g = 265$  °C) based on asymmetric biphenyl dianhydride (a-BPDA) by FDM with 80 °C higher use temperature than commercial Ultem 9085 ( $T_g = 186$  °C) [1]. Additionally, Ultem 1000 and its corresponding chopped fiber composites have been manufactured into parts by FDM [2]. Laser sintering of polyamides, such as polyamide 12, with use temperature ranged from 150-185 °C are well known [3, 4]. Even PEEK with melting temperature of 343 °C (use temperature = 173 °C) can be manufactured into 3D objects by a more elaborate LS process [5]. However, to the best of our knowledge, there is no report in the literature on the laser sintering of thermoset resins other than epoxy coated polyamides, metals or ceramic powders. The incentive of developing LS process for thermoset resins lies in the possibility of raising use temperature to 250-300 °C for 3D-printed objects, and the potential prospect of printing polymer carbon fiber composites for aerospace applications.

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The goal of this project is to investigate laser sintering of a melt of thermoset RTM370 imide resin with the reactive 4-phenylethynylphthalic (PEPA) terminal group, hoping to produce objects with higher use temperature between 250-300 °C. RTM370 resin has been infused into carbon fiber preforms to produce composite panels by resin transfer molding (RTM) [6] and resin film infusion (RFI) [7] for 288 °C aerospace applications. Therefore, it is envisioned that RTM370 could be melted and cured by LS to manufacture 3D objects, and then subsequently postcure to achieve additional crosslinking at 350-370 °C for long-term 288 °C aerospace applications. This paper presents a lesson learned from the rudimentary LS process for a thermoset RTM370 imide resin.

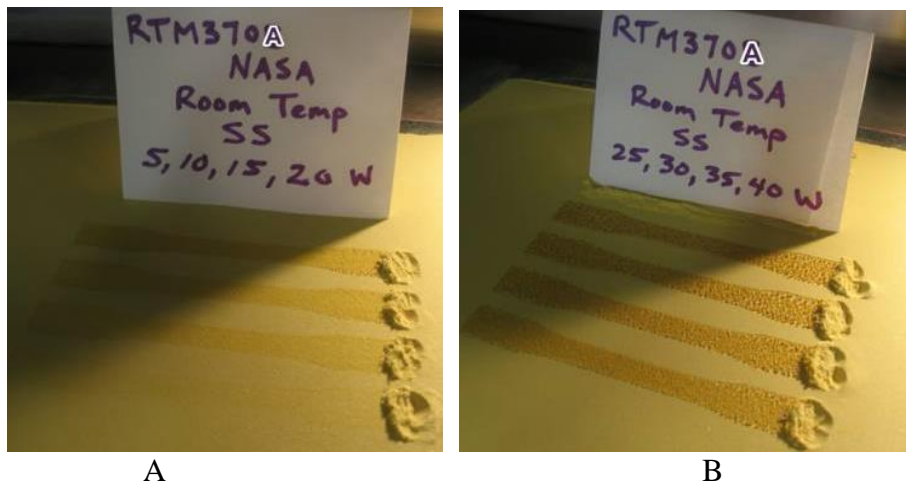
## 2. EXPERIMENTATION

RTM370 imide resin was ground into fine powder with particle size distribution ranging from 25-100 µm suitable for laser sintering. The laser sintering was conducted at the Rapid Prototyping Center at University of Louisville, KY, using a 3D Systems (Previously DTM) 2500plus machine that has been upgraded with both the Multizone Heater and high speed scanning kits from Integra Services International (Texas). The part bed area was filled with RTM370 resin powder, leveled with the roller and subsequently preheated to the target temperature and held for 15-30 minutes prior to scanning. Initial processing conditions were evaluated by scanning single layers of tensile specimens at varying scanning parameters such as laser power, scan speed, number of scans and scan spacing (spacing between adjacent scans). Part bed temperatures and scanning parameters were modified in an effort to determine the optimum settings for the material.

## 3. RESULTS AND DISCUSSION

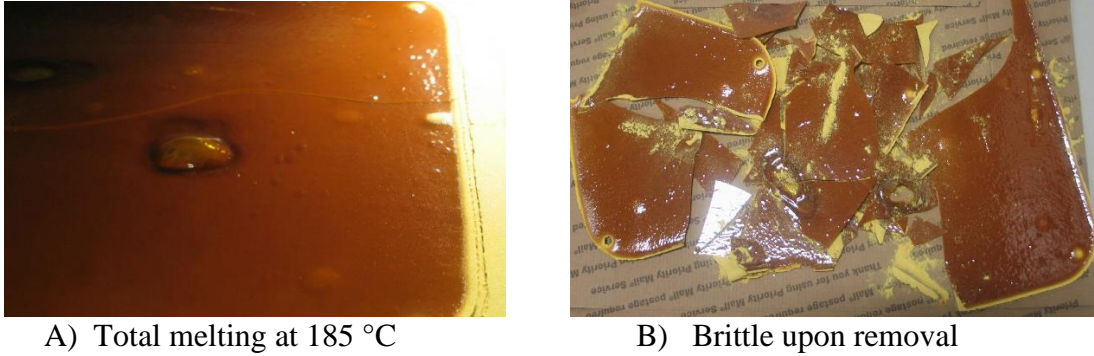
### 3.1 Searching for Laser Sintering Parameters and Conditions:

Single layers of tensile specimens were scanned at laser powers of 5, 10, 15, and 20W at 0.015 cm (0.006 in) scan spacing and scan speed of 508 cm/s (200 in/sec) at room temperature. There was insufficient energy to bond the particles into a layer for removal (Fig. 1A). The experiment was repeated but the laser powers were raised to 25, 30, 35, and 40W and the scans performed. Again the material did not melt and flow but instead balled, creating molten spheres that cooled rather than flowing into a sheet (Fig. 1B).



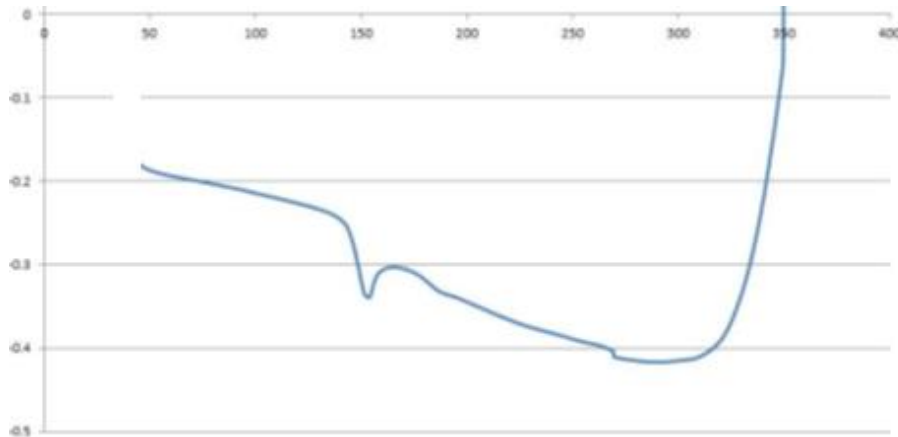
**Figure 1. Single scan of laser sintering of RTM370 resin at room temperature**  
(Scan rate = 508 cm/sec, scan spacing = 0.015 cm)

The part bed temperature set point was then set to 200 °C. However, the entire part bed started to melt and form a very smooth layer at a part bed temperature of near 185 °C (Fig. 2A) during the warm up to the set point. Upon removal from the machine, the solid part bed exhibited very brittle tendencies (Fig. 2B).



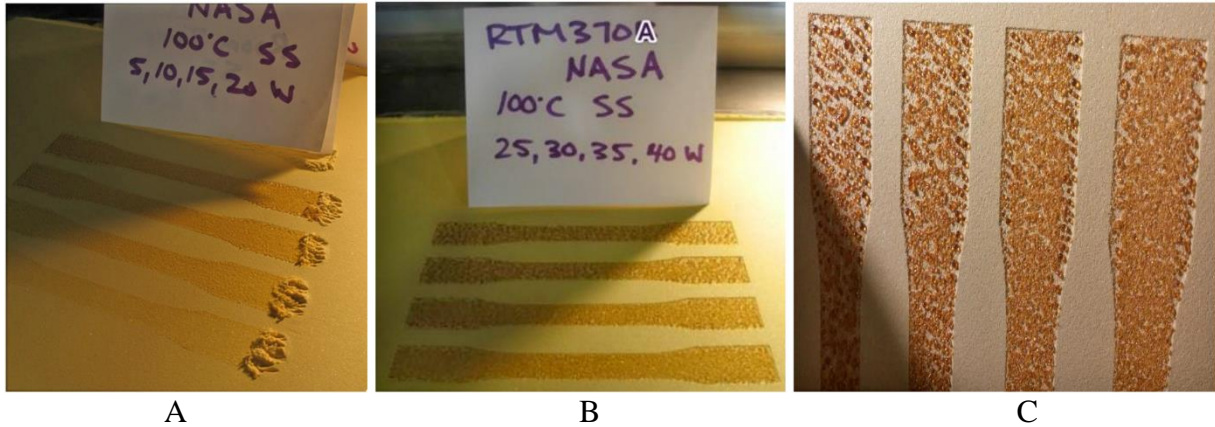
**Figure 2. Laser sintering of RTM370 at 185 °C bed temperature**

To determine the desirable bed temperature for LS, Differential Scanning Calorimetry (DSC) was performed on the RTM370 resin (Lot A). Fig. 3 shows that a sharp melting enthalpy change started at about 150 °C. It was decided that the part bed temperature would be dropped to 100 °C to determine the impact of a heated bed.



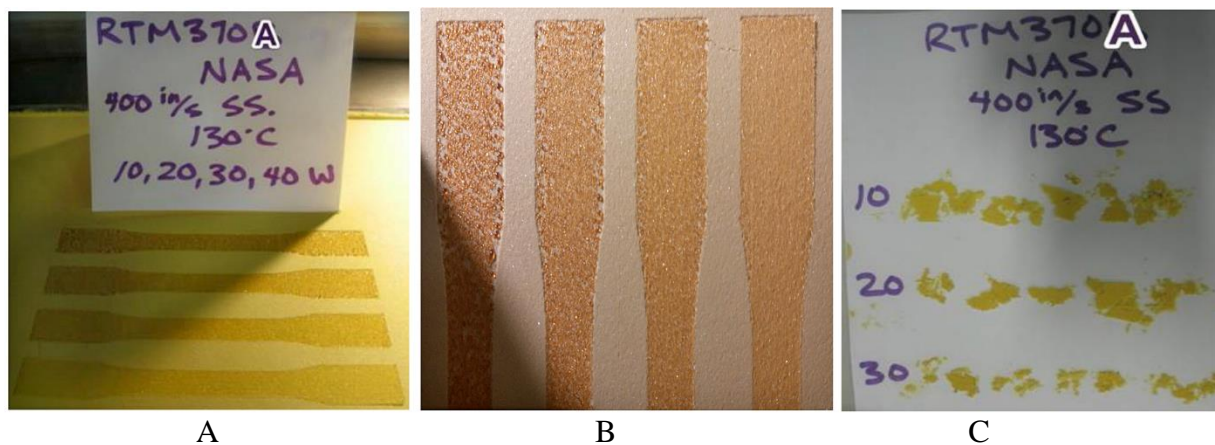
**Figure 3. DSC curve of RTM370 lot A**

The part bed temperature was set to 100 °C and single layers of tensile specimens scanned at laser powers of 5, 10, 15, and 20W at 0.015 cm (0.006 in) scan spacing and 508 cm/s (200 in/s) scan speed. These energy densities did not provide sufficient power for layer agglomeration (Fig. 4A). The experiment was repeated with laser powers of 25, 30, 35 and 40 watts (Fig. 4B). Balling was very evident in the 35W and 40W samples, and there was still no melt and flow in any of the samples (Fig. 4C)



**Figure 4. Single scan of LS at 100 °C: A) 10, 15, 20 Watts; B) 25, 30, 35, 40 Watts,**  
 (Scan rate = 508 cm/s, scan spacing = 0.015 cm)

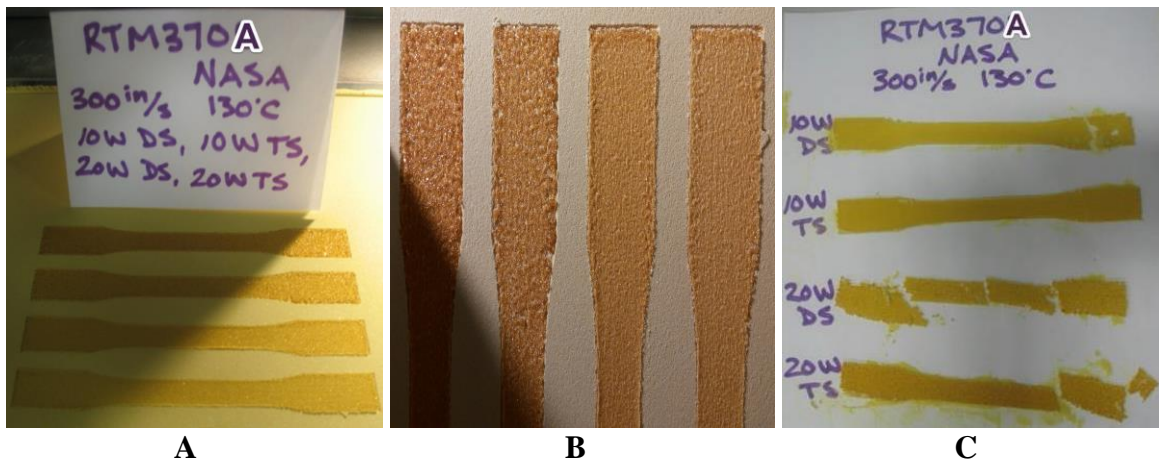
It is known that balling is due to surface energy and is generally decreased by increasing the scan speed and increasing the part bed temperature. The part bed temperature set point was increased to 130 °C and the scan speed to 1016 cm/s (400 in /sec). Single scans of 10, 20, 30 and 40W were performed. As can be seen in Fig. 5, there was some particle agglomeration in this test case (Fig. 5A). A close up of the ends of the samples showed that the lower two wattages on the right appear to provide some agglomeration without balling (Fig. 5B). Balling is still seen on the higher wattages. Some portions of the samples could be removed from the part bed (Fig. 5C). It is evident that the combination of the lower laser power and higher scan speed created what seems to be the most dense parts. However, as noted by the lack of color change indicating fusion, the particles appeared semi-sintered but did not fully melt.



**Figure 5. Single scan of LS at 130 °C with 10, 20, 30, 40 watts**  
 (Scan speed = 1016 cm/s = 400 in/s, scan rate = 0.015 cm)

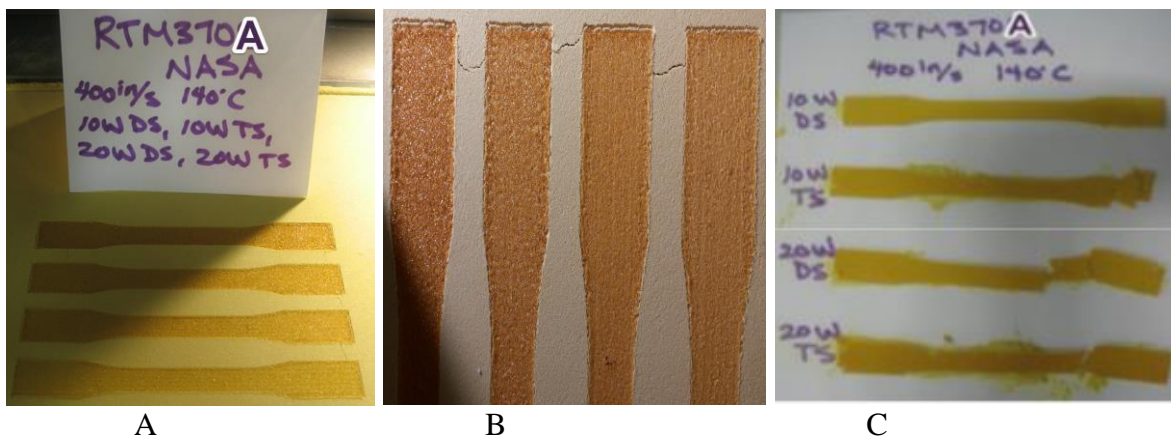


The material was re-leveled in the part bed, inerted, and preheated to 130 °C. The specimens were double and triple scanned at 10W and 20W with a scan speed of 762 cm/s (300 in/s). All 4 combinations did produce particle agglomeration. As can be seen from the image below (Fig. 6A) the triple scanned parts (20W triple scanned is the first on the left and the 10W triple scanned is the third from the left) appear to provide a more complete fusion. It can be noted from the color change in the 20W triple scanned part that there is melt of the material (Fig. 6B). Although the single layer scans could be removed from the part bed, the triple scanned parts seemed to hold together in a more rigid fashion (Fig. 6C).



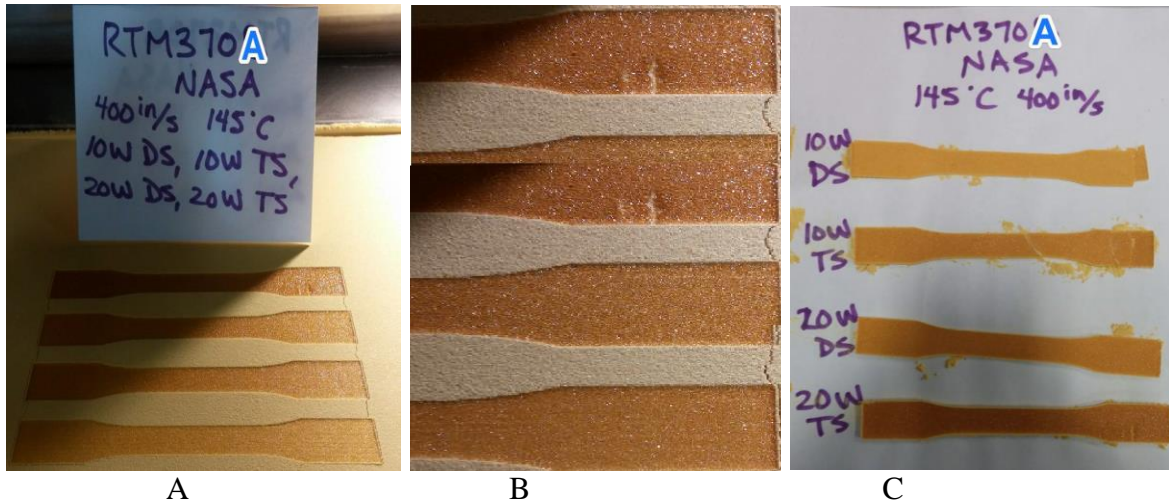
**Figure 6. Multiple scans of RTM370 at 130 °C with 10 and 20 watts**  
(Scan rate = 762 cm/s = 300 in/s, scan spacing = 0.015 cm)

The part bed temperature was raised to 140 °C. The scan speed was increased to 1016 cm/s (400 in/s) and the samples double and triple scanned at 10W and 20W (Fig. 7A). It appears that the higher scan speed and higher temperature gave more consistent, complete scans (Fig 7B) than the previous case. These combinations produced parts that could be removed from the machine but were still brittle (Fig. 7C).



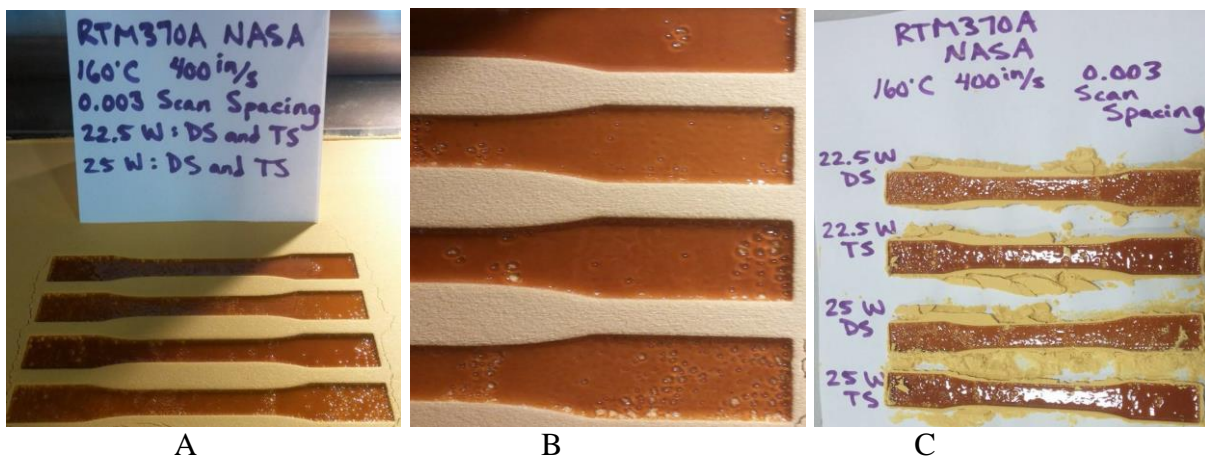
**Figure 7. Multiple scans of RTM370 at 140 °C with 10 and 20 watts**  
(Scan rate = 1016 cm/s = 400 in/s, scan spacing = 0.015 cm)

The part bed temperature was then raised to 145 °C and the specimens double and triple scanned at 10W and 20W as in the previous experiment. The higher temperatures produced slightly more dense parts (Fig. 8A). The lower wattages did not fully melt the powder. At 20W triple scanning some melting is starting to show but the particles are not fully melted (Fig. 8B). The specimens can be removed with integrity (Fig. 8C), but the powder bed was still not agglomerated, which would allow for powder reuse.



**Figure 8. Multiple scans of RTM370 at 145 °C and 10, 20 watts**  
(Scan rate = 1016 cm/s = 400 in/s, scan spacing = 0.015 cm)

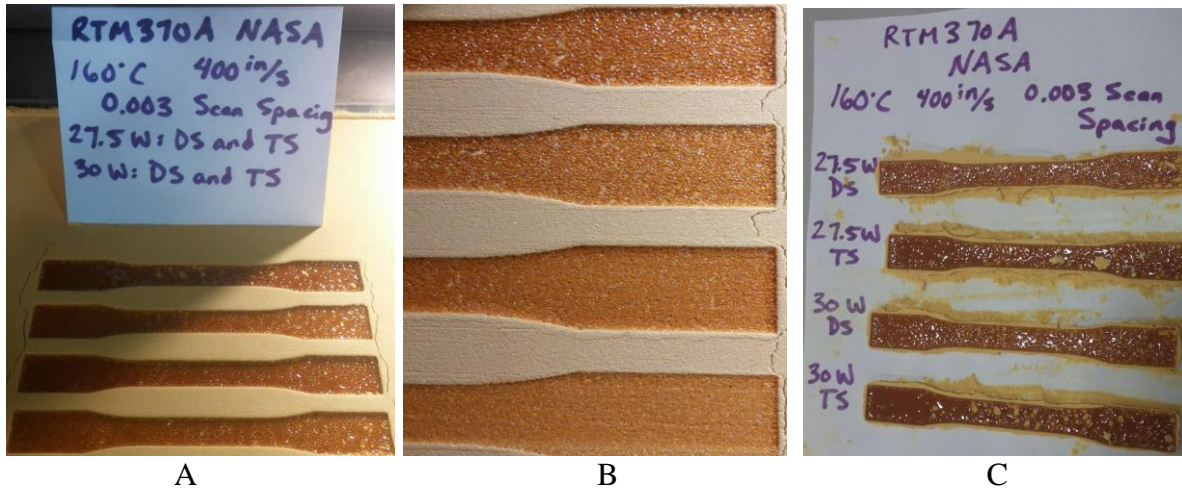
The part bed temperature was next raised to 160 °C. The scan spacing was decreased to 0.0076 cm (0.003 in) and the experiment performed with a scan speed of 1016 cm (400 in/s) and laser powers of 22.5W and 25W (Fig. 9A). Full melting and flow of the material is starting to occur at these settings. The triple scanned parts at both laser powers appeared similar and were smooth (Fig. 9B). There are some voids in the scans, but the specimens can be removed from the powder bed (Fig. 9C).



**Figure 9. Multiple scans of RTM370 at 160 °C with 22.5, 25 watts**  
(Scan rate = 1016 cm/s = 400 in/s, scan space = 0.0076 cm = 0.003 in)



The part bed temperature was kept at 160 °C. The scan spacing was held at 0.076 cm (0.003 in) and the experiment repeated with laser powers 27.5W and 30W (Fig.10A). Full melting and flow of the material occurred (Fig.10B). However, it appears as if these energy densities are above the optimum range as significant "spider webbing" and voids are evident in all of the scans (Fig.10C). This would be the best starting conditions for the construction of tensile specimens. However, there is insufficient powder remaining to conduct any more experiments on this particular batch of material. It may also be beneficial if the viscosity of the material was increased somewhat. The various LS conditions and the resultant specimen appearance are summarized in Table 1.



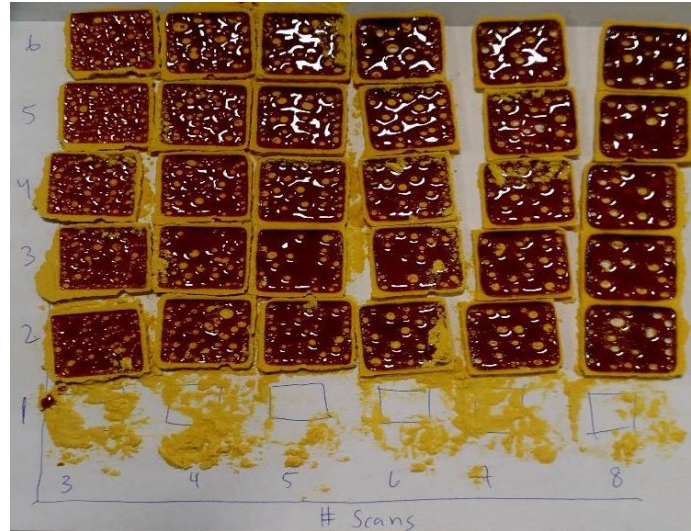
**Figure 10. Multiple scans of RTM370 at 160 °C with 27.5, 30 watts**  
(Scan rate = 1016 cm = 400 in/s, scan spacing = 0.0076 cm = 0.003 in)

**Table 1. Summary of LS Conditions and Specimen Appearance**

Bed Temp.	Power (Watts)	Scan Speed	Scan Spacing	Specimen Appearance
RT	5, 10, 15, 20 25, 30, 35, 40	508 cm/s (200 in/s)	0.015 cm (0.006 in)	Balling, cooled molten spheres, no melt flow
100 °C	5, 10, 15, 20 25, 30, 35, 40	508 cm/s (200 in/s)	0.015 cm (0.006 in)	Balling, cooled molten spheres, no melt flow
130 °C	10, 20, 30, 40	1080 cm/s (400 in/s)	0.015 cm (0.006 in)	Some agglomeration at 10, 20 Watts Balling at 30, 40 Watts
130 °C	10W, DS, TS 20W, DS, TS	762 cm/s (300 in/s)	0.015 cm (0.006 in)	20W/TS; some fusion and melt Specimens removable
140 °C	10W, DS, TS 20W, DS, TS	1080 cm/s (400 in/s)	0.015 cm (0.006 in)	Better fusion and melt Specimens are removable, hold better
145 °C	10W, DS, TS 20W, DS, TS	1080 cm/s (400 in/s)	0.015 cm (0.006 in)	Some melting, but no fully agglomeration Specimens fully removable
150 °C	10W, DS, TS 20W, DS, TS	1080 cm/s (400 in/s)	0.015 cm (0.006 in)	No full melting, but density increases Specimens fully removable
160 °C	22.5W, DS, TS 25W, DS, TS	1080 cm/s (400 in/s)	0.0076 cm (0.003 in)	Full melting and flow started to occur Specimens fully removable with spider web
160 °C	27.5W, DS, TS 30W, DS, TS	1080 cm/s (400 in/s)	0.0076 cm (0.003 in)	Full melting and flow occurred Specimens fully removable with voids

### 3.2 Attempted Crosslinking by Postcure:

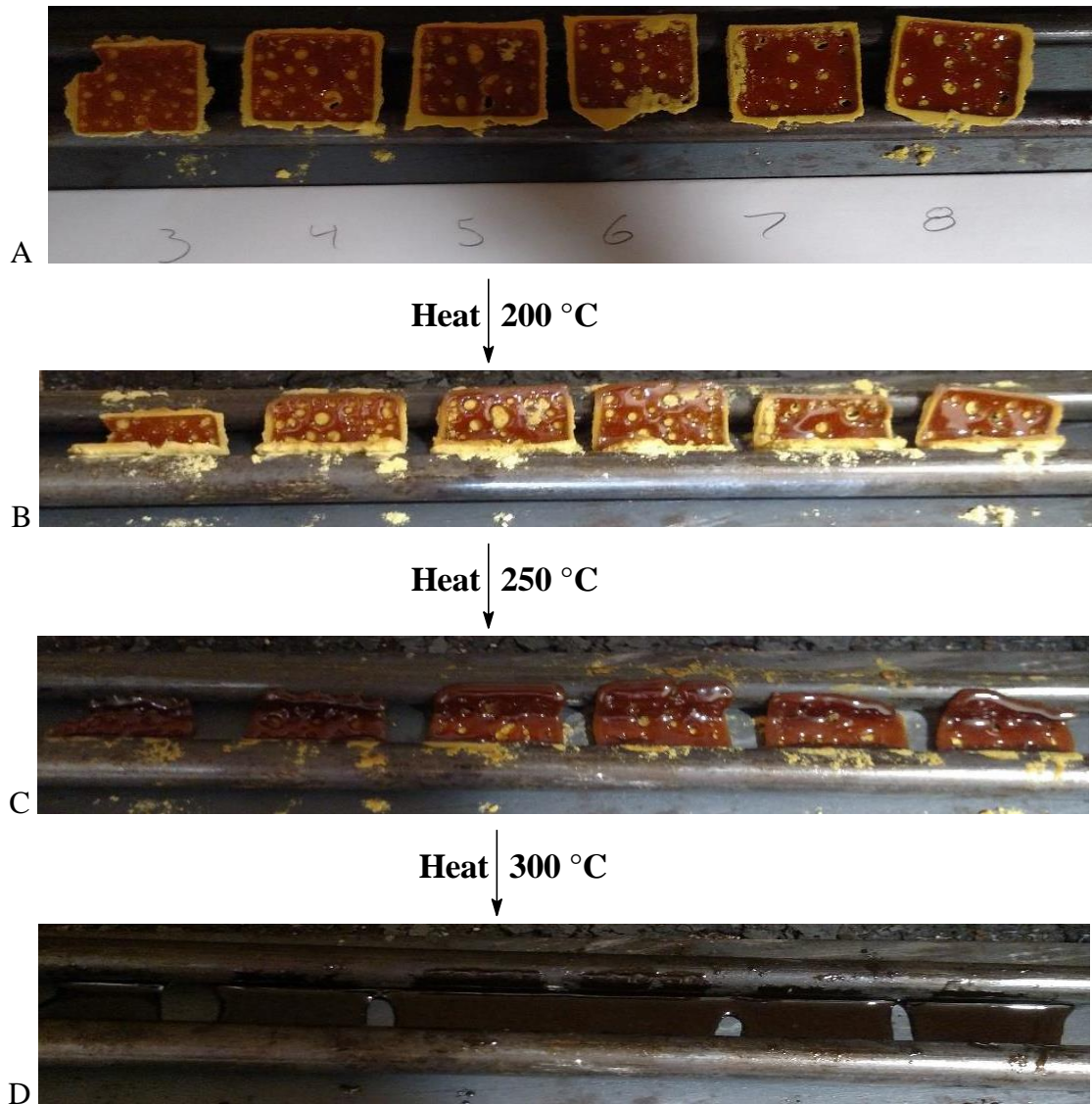
To conserve the resin materials used for LS, small 1inch squares were printed instead of tensile dogbone specimens at a part bed temperature of 160 °C. The single layer chips showed increased thickness and more melt as the number of scans increased from 3 to 8 at 27.5W laser power at 1016 cm/s (400in/s) scan speed and 0.0076 cm (0.003 inch) scan spacing (Fig. 11).



**Figure 11. Multiple Scans (3-8 scans) of RTM370 resin chips at 160 °C**  
(Scan rate = 1016 cm/s = 400 in/s, scan spacing = 0.0076 cm = 0.003 in)

One each of the chips for each scan multiples were then supported on rods in an oven (Fig. 12A) to see if there was any variation that might indicate that some crosslinking may be occurring in the LS equipment. The oven was heated to 200 °C and allowed to equilibrate. It appears as if all of the chips reacted similarly in that they did not hold their shape and sagged. However, they did not show signs of melting (Fig. 12B). The temperature was then raised to 250 °C and melting was starting to occur in all of the chips (Fig. 12C). It does appear as if more melting may have occurred in the lowest scan multiple chips. The temperature was further raised to 300 °C, and all of the chips at this temperature melted completely and flowed to form a solid sheet (Fig. 12D).

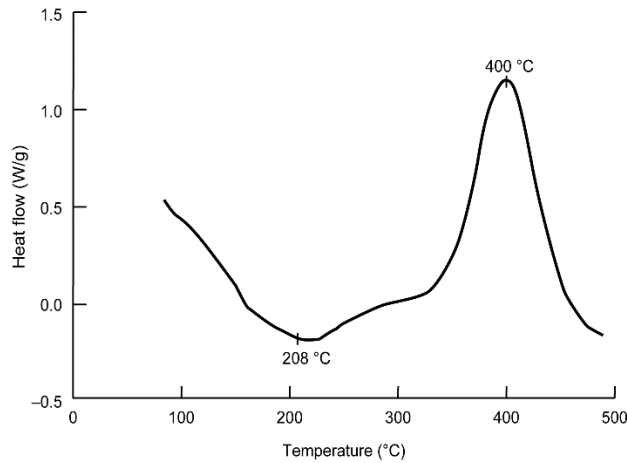




**Figure 12. Resin chips with multiple scans subjected to postcure in an oven**

### 3.3 Differential Scanning Calorimetry (DSC) Analysis:

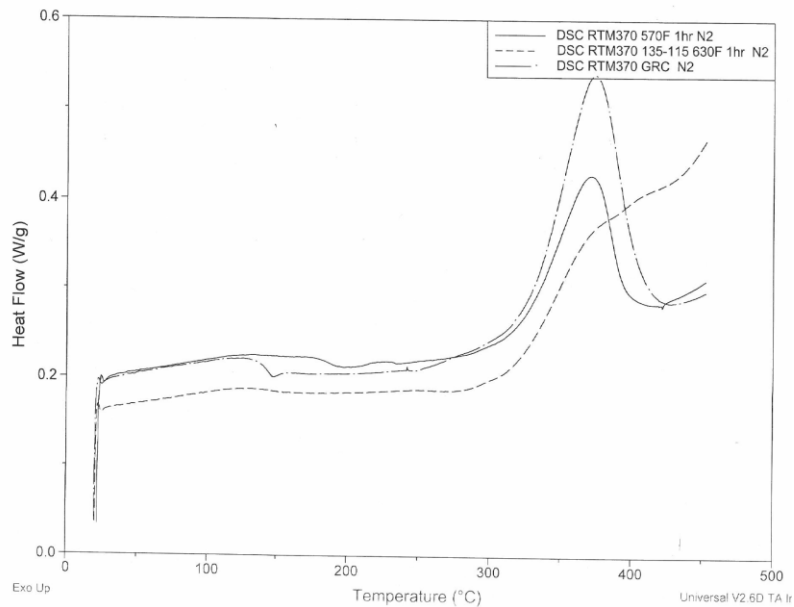
DSC trace of solid chips scanned 8 times with 27.5 Watts at a bed temperature of 160 °C by LS still exhibited a melting at 208 °C and a significant intensity of phenylethynyl curing exotherm at 400 °C (Fig. 13), indicating the lack of curing/crosslinking by the laser. This observation is consistent with the total melting of LS build chips without integrity in an oven heated above 250 °C. It is speculated that there is either not enough power or time for the laser to dwell on the specimens in fast scans to cure the phenylethynyl groups which normally cured at 371 °C under pressure for 1-2 hours.



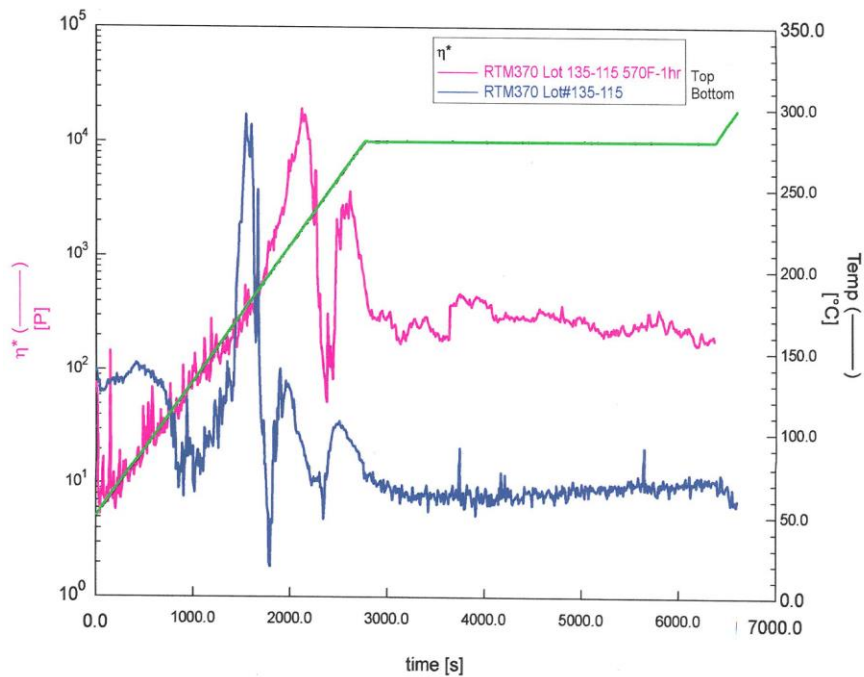
**Figure 13. DSC thermogram of RTM370 resin chips produced by 8 LS scans**

### 3.4 Future Work

Since the laser was only able to melt RTM370, but incapable of promoting the cure of PEPA terminal groups, a curing study of RTM370 resin was conducted to investigate the extent of cure with advance staging before the resin is subjected to LS. When RTM370 was further staged at 299 °C (570 °F) for 2 h, DSC analysis in Fig. 14 shows that the PEPA endcap was 50% cured whereas further staging at 332 °C (630 °F) totally cured the PEPA endcap. The rheology profiles (Fig. 15) also showed that the complex viscosity ( $\eta^*$ ) increased from initial 10 poise to ~200 poise after further staging at 299 °C (570 °F) for 1 h. The idea for future work is using further staging to promote either chain extension or crosslinking to increase the molecular weight and viscosity that are more resemble thermoplastic melting for LS to avoid excess melt-flow and enhance integrity of 3D-printed chips.



**Figure 14. DSC thermogram of RTM370 resin after pre-staging at 299 °C (570 °F) and 310 °C (630 °F)**



**Figure 15. Rheology of as-received RTM370 vs further staged at 299°C (570°F) for 1h**

#### 4. CONCLUSION

This project was initiated to determine whether laser sintering can be applied to high temperature thermoset polyimides to enhance covalent bonding between layers through the curing of the reactive endcaps, as compared to conventional thermoplastic polymers which display poor z-directional mechanical properties. Laser sintering was conducted on a melt-processable thermoset imide oligomer RTM370 for which composites manufactured by resin transfer molding (RTM) or resin infusion (RI) have been shown to exhibit outstanding mechanical property retention and good microcrack resistance at 288 °C (550 °F). Tensile specimens of RTM370 can be produced by laser sintering as the resin melt with 25-30 watts at 1016 cm/s (400 in/s) scan rate and 0.0076 cm (0.003 in) scan space in a bed temperature of 160 °C. However, the resultant dogbone specimens are brittle because of low molecular weight and sparse crosslinking of the melted oligomers. Attempted postcure on the LS-printed resin chips was unsuccessful, due to the melting of the chips instead of promoting additional crosslinking. DSC analysis showed that the laser scans only melted the oligomer resin, but fail to achieve crosslinking of the reactive PEPA endcap. Current planning for future work concentrates on pre-staging of RTM370 oligomer resin at 300-310 °C to promote either chain extension or crosslinking to increase the molecular weight and viscosity that are more resemble thermoplastic melting for LS to avoid too much melt-flow to help consolidating of 3D-printed RTM370 specimens. Increasing the laser dwelling time in hope of promoting crosslinking to enhance integrity of LS-printed tensile specimens will also be considered. Ultimately, the development of laser-curable reactive endcaps would be a viable solution to advance the laser sintering of thermoset resins in additive manufacturing for aerospace applications.



## 5. ACKNOWLEDGMENTS

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