Manufacturing of Thermoset Polyimide Composites by Laser Sintering

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Abstract

Selective Laser Sintering (SLS) 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 computer-aided design (CAD) model. SLS generally uses thermoplastic polymeric powders such as polyamides. The resultant 3D-printed objects are often weaker in their strength compared to traditionally processed materials, due to their higher porosity. This paper described the process development of using melt-processable imide oligomers terminated with reactive 4-phenylethynylphthalic anhydride (4-PEPA) to conduct laser sintering (LS). The first successful 3D-printing of high temperature RTM370 thermoset polyimide carbon fiber composites were further post-cured to promote additional crosslinking for achieving higher temperature (T_g = 370°C) capability. Another novel imide oligomer, RTM385-SLS, formulated with a complex melt viscosity [η*] of ~10^4-10^5 poise is also suitable for LS. RTM385-SLS resin powder was mixed with 20-25% of hexagonal boron nitride (h-BN) and subjected to LS to print out "Green" specimens which could be further post-cured to afford a thermally conductive but electrically insulating composites with high T_g of 385 °C. The cured composite specimens were then subjected to mechanical testing, thermal conductivity and porosity measurements as well as SEM characterization.

1. INTRODUCTION

Selective laser sintering (SLS) is an additive manufacturing technique that builds 3D models by using a laser to selectively melt cross sections in powdered polymeric materials layer by layer, following the slice of each computer-aided design (CAD) scan (Fig.1a). The commonly used polymers for SLS are polyamide powders with use temperature ranged from 150-185 °C [1-2]. Recently semi-crystalline PEEK of varied LS-grade powder with melting temperature (T_m) of 343-370°C, had to be heated up to 380°C to be manufactured into 3D objects by a more elaborate high temperature LS (HT-LS) machine and process to afford products with glass transition temperature (T_g) of 150 °C [3-4]. However, the 3D objects build by these thermoplastic polymers are often weak in their strength relative to traditionally processed materials, due to higher porosity and lack of polymer inter-chain connection in the z-direction. Therefore, the real incentive of developing a LS process for thermoset resins lies in the potential of 3D-printing objects with 250-300°C use temperature, and the prospect of printing polymer composites for aerospace application.

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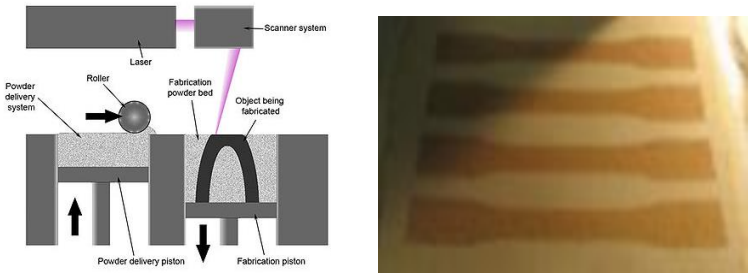


(a) (b)

Figure 1. Laser sintering of thermoset polyimide resin

The original idea was to conduct laser sintering (LS) using a melt-processable RTM370 imide resin (cured T_g = 370°C) terminated with reactive phenylethynyl (PEPA) group (Fig. 1b) that was originally designed for resin transfer molding (RTM) due to its low complex viscosity [η*] of 30 poise at 280°C. It was envisioned that RTM370 resin powder could be melted and cured by LS to manufacture 3D objects, and then subsequently post-cured to achieve additional crosslinking for >300°C aerospace applications. However, the viscosity originally designed for RTM application of 30 poise is too low for laser sintering, generating voids called spider webbing in the LS-printed dogbone specimens [5]. Therefore, RTM370 resin (RTM grade) had to be heated at 300°C for additional 2-3 hours to promote chain extension while avoiding extensive crosslinking of the PEPA endcaps before subjecting to laser sintering (LS).

2. EXPERIMENTATION

RTM370 (SLS grade) and RTM385-SLS resins were manufactured by Imitec Inc. in Schenectady, NY. RTM370-SLS is subjected to additional 2-3 hours of heating at 300 °C before grinding into powder as compared to RTM370-AG originally designed for RTM application. RTM385-SLS is also different from RTM385-AG designed for RTM use. Short carbon fibers (length ~60 μm) was obtained from Advanced Laser Materials, LLC (now part of EOS North America). Carbon fiber (35 wt%) was added to the RTM370 resin and then dry blended in a rotating drum tumbler to ensure a consistent blend. Hexagonal boron nitride platelets (h-BN, 30 μm, 98.5% pure) were purchased form American Elements. RTM385-SLS resin and h-BN were dry blended by ball milling to achieve a homogeneous powder mixture. To save the materials used for this LS study, SinterStation 2500 was retrofit with a small 10 cm × 10 cm build chamber (Fig. 2) out of the original build piston. Both the build piston/cylinder and the feed cartridges would need to be modified. The temperature of the part bed is monitored and controlled by an infrared sensor. The temperature of the feed cartridge is also measured by a thermocouple. The dogbone subscale specimens were 3D-printed by the laser following ASTM D368, Type V specification. The rheology was performed in the parallel plate geometry with 1g of imidized powder at a ramping rate of 4 °C/min and frequency at 10 rad/sec, using an Ares Rheometer. Differential scanning calorimetry (DSC) was conducted on TA Instruments Q1000 with 5 °C/ min. heating rate. The thermal conductivity was determined by modified transient plane source (MTPS) method using C-Therm TCi thermal conductivity analyzer. AccPyc II Pycnometer by Micromeritics was used to measured porosity in LS disk.

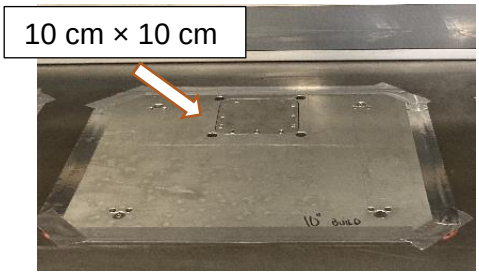


Figure 2. A small build chamber (10″ ×10″)

3. RESULTS AND DISCUSSION

Part I: Manufacturing of Thermoset Polyimide Carbon Fiber Composites by Laser Sintering

3.1 Laser Sintering of RTM 370 Resin:

Our initial attempt to produce durable resin chips and dogbone specimens by LS using the original RTM370 powder designed for RTM application with ~30 poise, but viscosity was too low for LS, generating voids (called spider webbing) in the LS-printed dogbone specimens [5]. Therefore, RTM370 resin (RTM grade) was further heated at 300 °C for additional 2.5 hours to achieve a higher viscosity, via chain extension through reactive PEPA endcaps while avoiding extensive crosslinking, as evidenced by the formation of a filaments inside the rheometer (Fig. 3). DSC thermogram showed a T_g of ~170 °C and a PEPA endcap curing at 372 °C (Fig. 4).

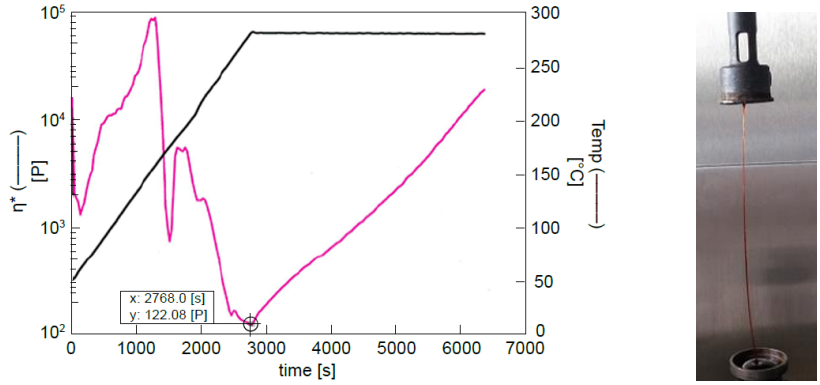


Fig. 3. Viscosity of RTM370 resin staged at 300 °C for 2.5 h and the filament formation

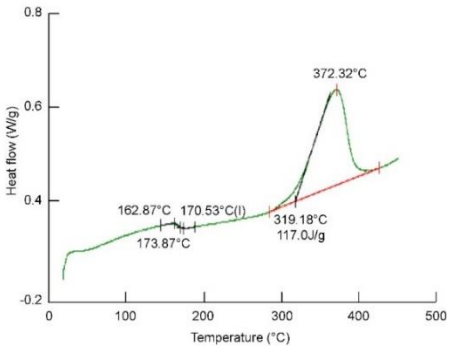
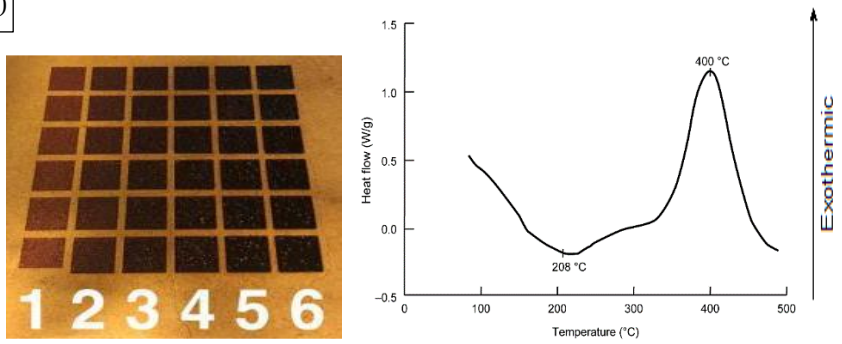


Figure 4. DSC of RTM370 resin after staging at 300 °C for 2.5 h

Using parameter listed in Table 1, several sets of 6 resin chips (1-6 scans) were produced by LS using further heated RTM370 resin, and they appeared very uniform (Fig. 5A). However, DSC thermogram of the 6-scans resin disk still showed significant amount of PEPA exotherm at 400 °C (Fig. 5B), indicating incomplete cure of the PEPA endcaps even after multiple laser scans.

Table 1. Parameter Set I

Part Bed Temperature: 180 °C Laser Power: 25W Scan Speed: 1016 cm (400 in/s) Scan Spacing :0.076 cm (0.003 in)



(A) (B)

Figure 5. LS-printed resin chips and DSC curve of 6-scans resin disk

3.2 Laser Sintering of RTM 370 /Carbon Fiber Composites [6]:

To improve the stiffness of the build layers, RTM370 resin was mixed with 35% carbon fibers (~60 µm in length) and dry blended for printing composite specimens by LS. The single layer square samples all scanned successfully (Table 2) and exhibited greater green strength (Fig. 6) than any of the neat resin scans in previous LS runs. It is believed that the thermally conductive carbon fibers not only provide the stiffness, but also significantly improve the heat transfer to the resin/fiber mixture on the powder bed upon irradiation by the laser. This phenomenon is also confirmed with the recent report that a thermoset bismaleimide resin was blended with thermally conductive carbon micro-balloons to increase its laser absorbability for a successful laser sintering [7]. The depth of penetration (chip thickness) also increased with increasing number of scans; however, DSC thermogram still showed substantial exotherm of the uncured PEPA endcap resemble to the situation shown in Figure 5B, indicating that the green composite disk of 6-scans was still not fully cured yet. The thermal conductivity of the carbon fiber-filled RTM370 LS disk in Fig. 7 (0.6 W/m.K, porous) is almost 3 times that of a neat resin disk (0.2 W/m.K, dense). The porosity of the LS disk is ~54% based on gas pycnometer measurement.

Table 2. Parameter Set II

Part Bed Temperature: 180 °C Laser Power: 25W Scan Speed: 1016 cm/s (400 in/s) Scan Spacing :0.0076 cm (0.003 in)

Figure 6. Carbon-fiber-filled RTM370 composite chips by LS

Figure 7. Carbon-fiber-filled LS-printed disk (left) and neat resin disk (right)

3.3 Laser Sintering of Composite Specimens:

A) <u>100 µm Thickness Layers</u>: With the success of producing the single scan composite chip with integrity, the objective shifted to focus on building composite specimens and parts by LS. The initial build parameters used is listed in Table 3.

Table 3. Parameter Set III

Part Bed Temperature: 180 °C
Feed Temperature: 90 °C
Layer Thickness: **100 µm (0.004")**
Laser Power: **25W**
Scan speed: 106 cm/s (400"/s)

A layer of material was spread across the build platform and heated up to the specified temperature to observe changes in state. During the addition of powder layer, the material was not rolling well in front of the roller/spreader but "bulldozing" instead. It was thought that the powder may be overheating due to the change in the location of the thermocouple to control the feed temperature. Over several build attempts, the feed temperature was dropped to 70 °C and the feed heater output limit was dropped from 60% to 20% to prevent the feed area from melting. If the temperature of the feed powder gets too high, it can cause the powder to agglomerate and/or melt. An indicator of the powder temperature getting too high is the feed bed "cracking" as shown in Fig. 8.

Figure 8. Composite feed bed cracking due to high heat

A few builds were attempted at these conditions, but in all cases the layers would shift as the roller/spreader assembly moved across the build area. The layer shifting can also be caused by shear forces generated between the previously melted layer and the new powder being applied to

the build area. This is most evident when the material does not roll easily and instead bulldozes. Layer shifting is shown below during the build and post build (Fig. 9).

Figure 9. Layers shifting during the build and post building

B) <u>125µm Thickness Layers</u>: To build thicker layers, the laser power was increased to 31W, (Table 4) and multiple runs of tensile bars were attempted. More layers could be successfully completed compared to the 100µ layer builds.

Table 4. Parameter Set IV

Part Bed Temperature: 180 °C
Feed Temperature: 90 °C
Layer Thickness: 125 µm (0.005")
Laser Power: 31.3W
Scan Speed: 1016 cm/s (400"/s)
Scan Spacing : 0.076 cm (0.003")
Number of scan: 2

The layer shifting was decreased; however, warping and curling was seen during the build. Curling is generally a temperature issue caused by non-uniform cooling that contributed to parts curling or warping like a banana in build area (Fig. 10). The part then "rocks" as the roller/spreader assembly moves across the part bed.

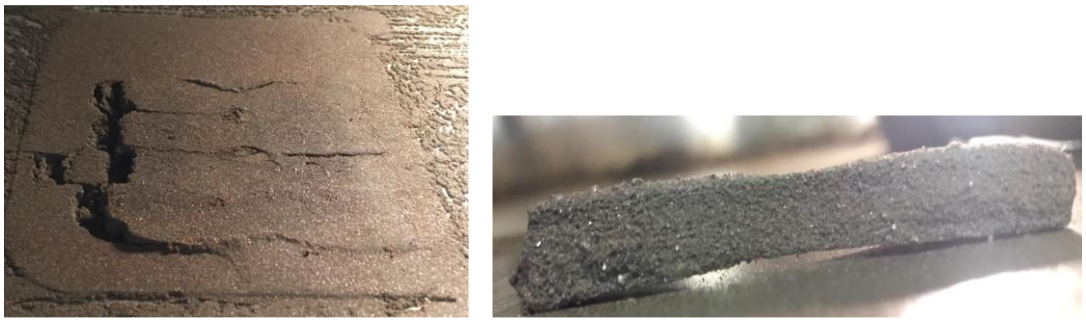


Figure 10. Warping during the build and sample curling post building

It was determined that the curling may be due to the lack of dedicated part piston and cylinder heating in the small build volume retrofit. The machine would be preheated for 2-4 hours at the

set temperatures to allow for all the metal parts to come to equilibrium and heat soak to minimize curling. While the curling was starting to be less visible, there was still layer shifting occurring.

C) 150 µm Thick Layers: The layer thickness was increased to 150 µm and the experiments repeated using increased laser power to 38W (Table 5). With the modified feed cartridge, it was difficult to keep the thermocouple precisely located to just below the surface of the powder. This resulted in issues with maintaining consistent feed temperature control. However, a few subscale tensile specimens (Fig. 11) for postcure and mechanical tests were successfully 3D-printed in addition to several round disks (25 mm diameter × 2 mm thick) and 0.6 cm cubes for characterization, using the parameters listed in Table 5.

Table 5. Parameter Set V

Part Bed Temperature:180°C
Feed Temperature: 90°C
Layer Thickness: 150µm (0.006 in)
Laser Power: 38W
Scan Speed: 1016 cm/s (400"/s)
Scan Spacing: 0.076 cm (0.003 in)

Figure 11. Tensile specimens during LS build process and after post build

D) Particle Size Analysis: A particle size analysis was conducted on the carbon fiber blended material. It was noticed that there were two new peaks appeared at 254 µm and 1054 µm (Fig. 12) after RTM370 resin powder (RTM grade) was further heated at 300°C for 3 hour compared to the original batch of RTM 370 powder with a single peak at 70 µm between 40-120 µm prior to further staging at 300 °C (Fig. 13). These are likely due to the agglomeration of resin particles after additional staging/heating as well as carbon fiber (length ~60µ) entanglement during the dry blending of the fiber with resin powder. The surface roughness of LS-printed composite specimens may be the result of uneven particle size distribution/agglomeration as compared to the more uniform neat LS disks. The layer thickness would be increased to account for the difference.

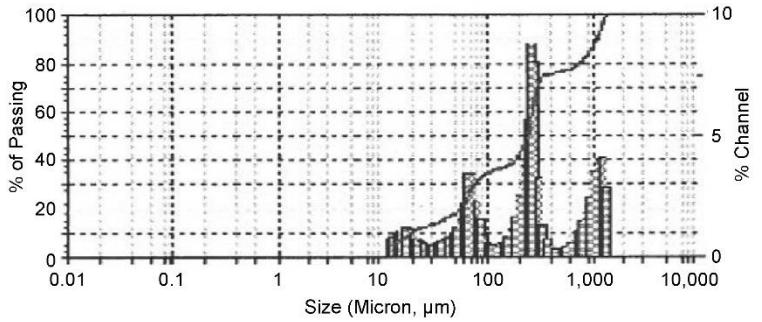


Figure 12. Particle size distribution of further staged RTM370 blended with milled carbon fiber

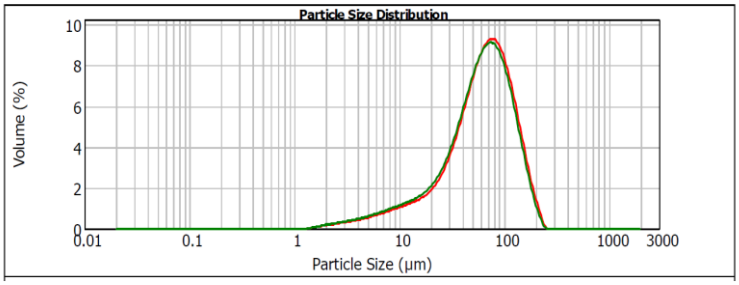
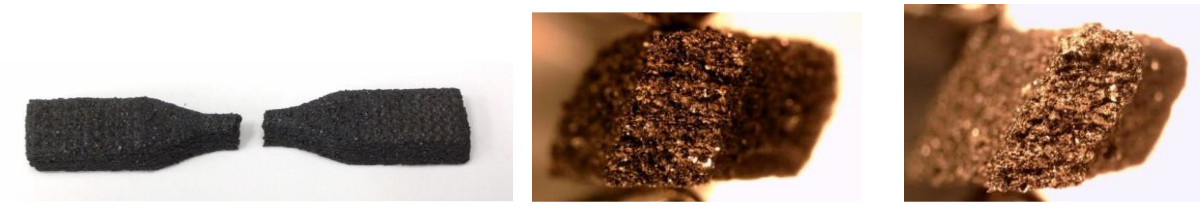


Figure 13. Original particle distribution of RTM370 for RTM process

3.4 Characterization of LS-Printed Tensile Specimens:

Half a dozen dogbones subscale specimens, ASTM D368, Type V [6.5 cm × 0.9 cm × 0.5 cm thick, neck width 0.3 cm], were printed following the protocol described in the above section. The as-print specimens were subjected to multi-step gradual temperature rise (3-5 °C/min) and constant temperature holds with final post-cure at 343 °C (650 °F) for 16 hours to complete total cure of PEPA endcaps and achieve optimal mechanical properties. A test speed of 0.127 cm/min (0.5 in/min) was used. The grip pressure was set to 1.38 MPa (200 psi). The furnace temperature was equilibrated and specimens were conditioned 15 min before testing. Test of dogbone specimens misbehaved when testing at room temperature. However, all tensile testing at 288 °C (550 °F) fractured nicely at the mid-section of dogbones (Fig.14a-c). SEM micrograph of the fractured LS-printed composite (Fig. 15) revealed milled fibers were incorporated into the LS-printed specimens. Furthermore, Table 1 indicated that the samples retained similar tensile strength at 288 °C as well as at room temperature (19 °C).



a) Gauge Fracture b) Fracture Surface c) Angled

Figure 14. Fracture surfaces of dogbone subscale tensile specimens

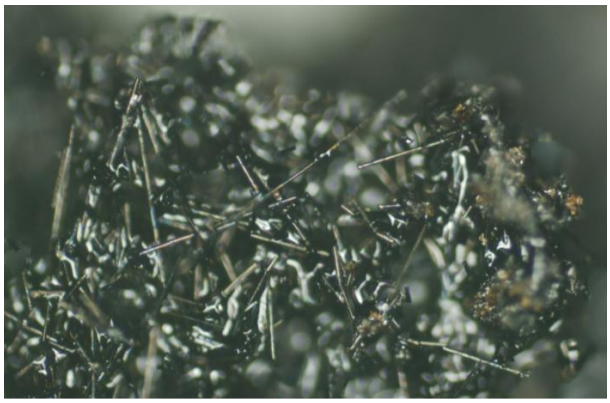


Figure 15. SEM micrograph showed milled carbon fibers at fracture surface

Table 6. Tensile Property of LS-Printed Specimens

Sample No.*	Test Temperature	Strength, (MPa)
A-1	**292 °C** (558 °F)	22.78
A-2	**289 °C** (552 °F)	28.09
B-1	**289 °C** (552 °F)	26.67
B-2	**287 °C** (549 °F)	26.22
Avg.		**26 ± 2**
C-1	**19 °C** (66 °F)	23.04
C-2	**19 °C** (66 °F)	26.09
Avg.		**25 ± 2**

Sample A, B, and C belongs to 3 different built lots of similar size and thickness

3.5. Laser Sintering of Composite Parts:

Following the success of printing composite specimens at 150 µm thick layers, efforts began to focus on printing subscale components such as a bracket, using the same parameters. Initially the bracket was attempted to be constructed at a 50% scale. The part was able to complete but the warping and shifting was too much to consider it a successful part. (Fig. 16A). Using longer heat soak times helped somewhat; however, to print a bracket in decent shape required full thermal control in piston and cylinder heater temperature control as well as the overhead part bed heating (Fig. 16B). Eventually, the 30% scaled geometric bracket was built well as a successful 3D-components by LS (Fig. 16C). The "Green" bracket was subjected to multi-step post-cure cycles by heating gradually at 3-5 °C/min from room temperature along with multiple holds at steady temperature for extended period of time and a final post-cure at 365 °C for 16 hours to complete the total curing of PEPA endcap to form a crosslinked network, while avoiding dimensional change due to softening at elevated temperature during the process. No noticeable dimensional change was observed in the post-cured parts. This is the first known high temperature polyimide composite parts (T_g = 370 °C) printed by laser sintering in additive manufacturing field that can be used for >300 °C aerospace applications.

A B C

Figure 16. Stages of composite brackets printed by LS

3.6. Summary of laser sintering of RTM370 carbon fiber composites

This project was initiated to determine if 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. A melt-processable RTM370 imide resin originally designed for resin transfer molding (RTM) [8] and resin film infusion (RFI) [9] was dry blended with 35 wt% finely milled carbon fibers and used as a feedstock for laser sintering. Using laser power of 25-38W and a bed temperature of 180 °C along with feed temperature of 80 °C, tensile specimens and subscale composite brackets were printed into green parts (not fully cured) by laser sintering successfully. The filled carbon fibers apparently impart not only the stiffness, but also higher heat transfer efficiency to enable building thicker layers, as compared to the neat resin in LS process. To complete total cure of the PEPA endcaps, the green parts were subjected to slow, multiple-stage post-cure to form a fully crosslinked network as the final parts appeared intact without any significant dimensional change. Essentially, a thermoset polyimide composite 3D network was achieved by using melt-processable imide oligomers terminated with reactive PEPA endcaps for LS processing. To the best of our knowledge, this paper demonstrates the first major advance in the additive manufacturing of high temperature thermoset polyimide composites with glass transition temperature (T_g) of 370 °C 3D-printed by LS. Another advantage of this breakthrough is that these thermoset oligomers can be 3D-printed by a regular laser sintering machine, without the need of using the high temperature laser sintering process (HT-LS, 250-380 °C) required for processing commercial thermoplastic PEEK with 150-185 °C use temperature.

Part II: Manufacturing of Thermally Conductive but Electrically Insulating Composites with Hexagonal Boron Nitride (h-BN) by Laser Sintering [10]

4.1 Laser sintering of RTM385-SLS neat resin

Based on the lesson learned from the laser sintering of RTM370 resin (cured T_g = 370°C), RTM385-SLS resin (cured T_g = 385°C) was specially formulated to display a complex melt-viscosity [η*] of ~10^4 -10^5 poise suitable for laser sintering. The rheology of RTM385-SLS oligomer powder shown in Figure 17 indicated the complex melt-viscosity [η*] was holding steady at ~50,000 poise at 280 °C for 1-2 hours. When RTM385-SLS was subjected to laser sintering at

the bed temperature of 180°C, it could be consolidated into resin disks between 25-38 W laser power, although the resin disks appear brittle (Fig. 18), because the reactive PEPA endcaps within the resin are not fully cured yet during the LS process.

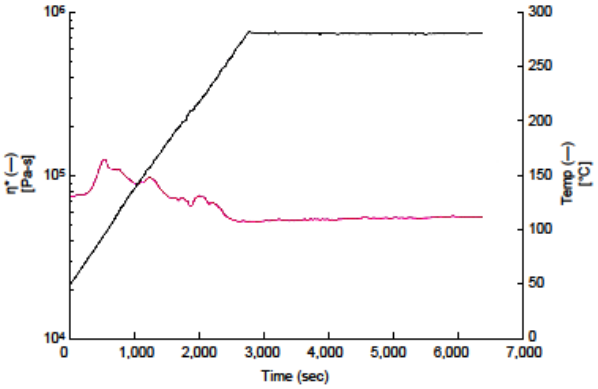
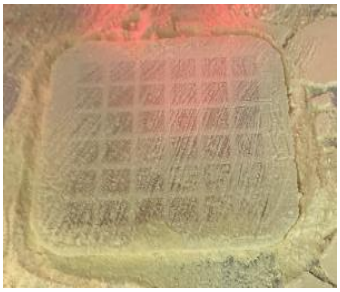


Figure 17. Rheology of RTM385-SLS imide oligomer powder

Scan Parameters
Bed Temperature: 180°C
Feed Temperature: 141°C
Laser Power: 25-38W
Scan Speed: 400 in/s
Scan Spacing: 0.003 in
Scan Count: 1 at 0.005 in



Inside powder bed

1-6 layers from right to left

Figure 18. Laser sintering of RTM385-SLS oligomer powder

4.2 Laser Sintering of RTM385-SLS with hexagonal boron nitride (h-BN)

Following the success of laser sintering of RTM385-SLS neat resin, ultimately the goal of this project is to print the RTM385-SLS filled with h-BN to afford the thermally conductive but electrically insulating composites for potential application for electrified aircrafts. As lesson learned from the previous LS project with RTM370 imide resin filled with finely milled carbon fibers, the thermally conductive fillers, such as carbon fibers or h-BN would enhance the laser absorptivity and the efficiency of LS process, due to higher thermal conductivity of the fillers.

Attempts to print 1-6 layers of 1cm by 1 cm disks using 20wt% of h-BN/resin at 25W laser power was not very successful as seen with 7 out of 36 disks unable to recover (Figure 19A). Increasing the laser power to 30W while keeping the same 20wt% h-BN/resin composition enhanced the integrity of the composite disks to which only a few disks crumbled (Figure 19B). To increase the thermal conductivity of the composites, 25wt% h-BN/resin was printed at 30W and only one disk crumbled out of 36 (Figure 19C). Based on the above observation, it is concluded that a better condition for printing out composite disks is using 25wt% h-BN/resin with 30W laser power. Previous compression molding study indicated that due to the large volume of h-BN, 30wt% ratio of h-BN/resin is too high to consolidate the resin with the h-BN effectively, so 25% h-BN was chosen for LS.

Scan Parameters: Temperature: 180°C; **Laser Power: 25-30W**; Scan Speed: 400 in/s; Scan Spacing: 0.003 in; Scan Count: 1 at 0.005 in

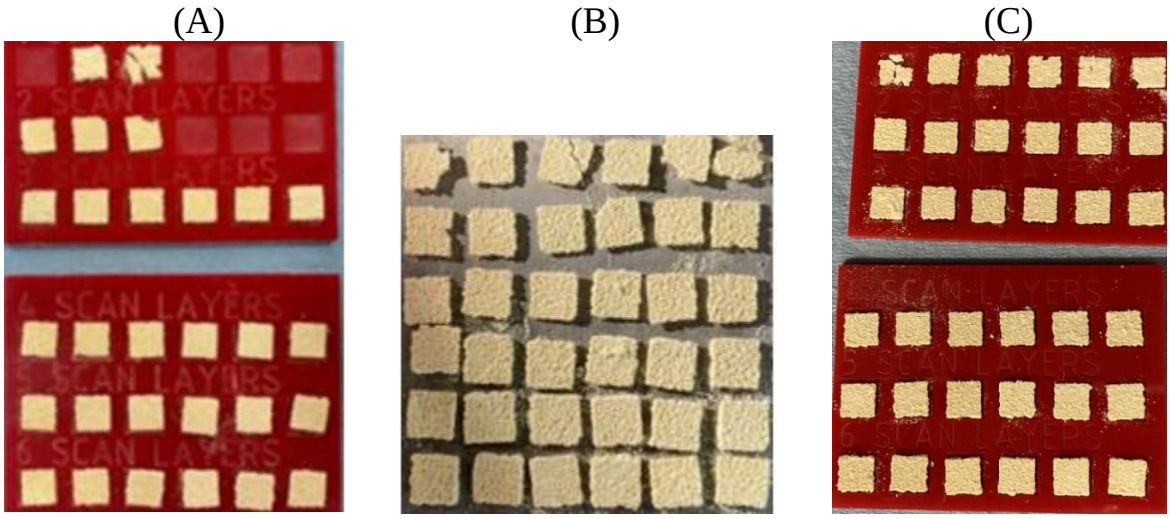


Figure 19. Laser sintering of BN/RTM385-SLS composite disks

DSC analysis was used to compare the PEPA endcap exotherm peak at 385°C between the RTM385 virgin neat resin and the RTM385-LS (laser sintered), Fig. 20 shows their normalized heat flow. The PEPA exotherm for the virgin RTM385 resin is 307.1 J/g as compared to that of 306.7 J/g for lasers-sintered resin at 30W, a very small difference of 0.4 J/g (< 0.2%). This indicates the reactive PEPA endcaps were only sparsely cured by the laser. The lack of PEPA crosslinking to build a 3D network in resin is the reason why the green h-BN composite disks and dogbones are so fragile.

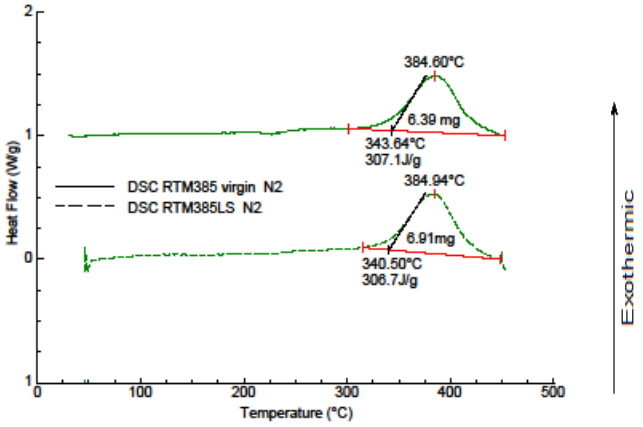


Figure 20. DSC thermograms of PEPA endcaps curing of RTM385 virgin vs RTM385-LS

The laser sintering of h-BN composite dogbones were carried out based on the success of 3D printing of h-BN composite disks using similar parameters. At 30W power, the dogbone texture seemed loosely consolidated and the neck broke off easily as shown in Fig. 21A. When the power was increased to 35W, the strength of the dogbone specimens improved for 25wt%BN/resin composites with only 1 out of 4 fractured necks and the texture appeared more consolidated,

although these "green" specimens are only partially cured (Fig. 21B). At 38W, 25wt% BN, about 1 out of 5 dogbones resulted in broken neck (Fig. 21C), but the 38W power sometimes had a tendency of excessively melting the resin. Attempts to use recycled 20wt% BN/resin from the powder bed resulted in a caked effect, indicating that recycled resin powder previously located in the peripheral of laser scan might have been slightly cured by the laser (Fig. 21D). Also, it seems that the composites filled with h-BN are more brittle than that of the milled carbon fiber which has a higher aspect ratio that offers entanglement to strengthen the composites.

Scan Parameters: Temperature: 180°C; **Laser Power: 30W-38W**; Scan Speed: 400 in/s; Scan Spacing: 0.003 in; Scan Count: 1 at 0.005 in

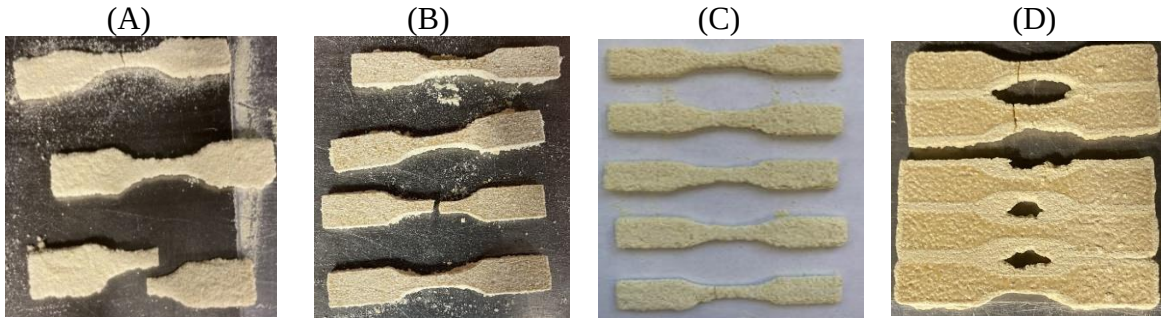


Figure 21. Laser sintering of BN/RTM385-SLS composite dogbone specimens

4.3 Analysis of post-cured 25wt% h-BN/RTM385-SLS composite specimens

The as-sintered h-BN composite dogbone specimens in Fig. 21(B-C) are post-cured in a blue M oven as follows: a) Ramped from room temperature to 232 °C (450 °F) over 2 hrs and then held at 232 °C for 2 hrs. b) Ramped from 232 °C to 343 °C (650 °F) over 8 hrs and held at 343°C for 16 hrs and then cooled. The post-cured dogbones specimens as shown in Figure 22 were subjected to thermal analysis and thermal conductivity measurement. The T_g of the post-cured 25wt% BN-PI composite is 395 °C as measured by thermal mechanical analysis (TMA). The thermal conductivity of the composite is ~0.7 W/m.K versus ~ 0.2W/m.K for the neat resin. The porosity of the composites as determined by pycnometry are between ~6-7%, which are considered very good in AM. SEM of post-cured dogbone specimens (Fig. 22) shows that h-BN platelets are evenly distributed throughout the LS-printed samples.

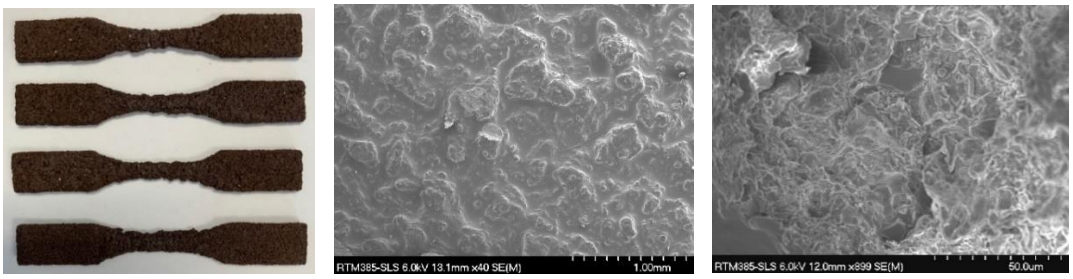


Figure 22. Photo and SEM of cured h-BN/RTM385-SLS composite dogbone surface

4.4 Mechanical testing of post-cured 25wt% h-BN/RTM385-SLS composite specimens

After post-cured at 343 °C (650 °F) for 16 hrs, the 35W LS-printed dogbones were subjected to mechanical testing. The elevated temperature testing faced some challenge as boron nititride acting as a lubricant while resin softening as the temperature raising, leading the dogbone specimens to slip out of the grip fixture sometimes. The mechanical strength of the 35W LS-printed dogbone specimens were presented in Table 7, as they generated a more consistent quality and data compared to the 38W-printed samples. The mechanical strength of the AM-dogbones at 250 °C are comparable to that of the ambient since the T_g of the composite dogbone is 395 °C. The zig-zag slim neckline of h-BN composite dogbone was the weakest link, even though the rest of the dogbone were bonded strongly and difficult to break. Therefore, it is advised that the h-BN/ resin powder may be suitable for 3D-printing solid parts, but not for very delicate components. Additionally, the tensile strength of these h-BN containing LS-dogbones (10-11 MPa) only exhibited about half of the strength relative to the carbon fiber-filled LS dogbones (25-26 Mpa) shown in Table 6. The reason is again due to the higher strength and higher aspect ratio of milled carbon fibers versus the more brittle h-BN platelets. Furthermore, SEM microscopy (Fig. 23) revealed that h-BN platelets are exfoliated in the mid-point fracture surface of the LS dogbones, which is astonishing as exfoliation often improved the thermal conductivity.

Table 7. Tensile Property of 35W LS-Printed Specimens

Sample No.	Test Temperature	Strength, (MPa)
LS-35W-1	Ambient	9.24
LS-35W-2	Ambient	10.11
Average	**Ambient**	**10 ± 1**
LS-35W-3	250°C (482 °F)	12.72
LS-35W-4	250°C (482 °F)	10.04
LS-35W-3	250°C (482 °F)	11.62
Average	**250°C (482 °F)**	**11 ± 1**

1) Test rate: 0.127 cm/min (0.5 in/min).
2) Vice clamps were used to grip the specimens instead of hydraulic grips.
3) Instru-Met 4505, 90/22 with 100KN capacity was used.

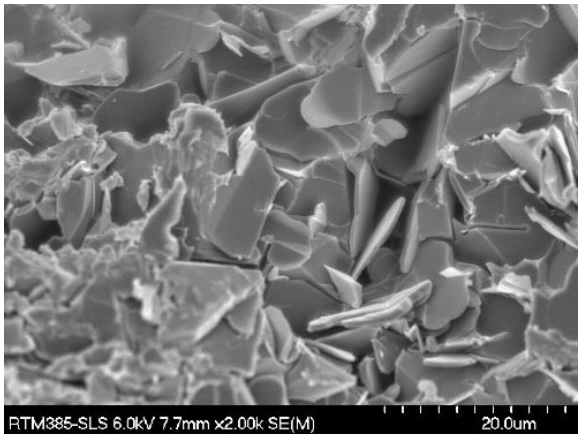


Figure 23. SEM micrograph of fracture surface of exfoliated h-BN platelets

5. CONCLUSION

This paper demonstrated the feasibility of using melt-processable thermoset RTM polyimide resins filled with milled carbon fibers or h-BN for additive manufacturing by laser sintering. Novel RTM370 (SLS grade) and RTM385-SLS with a complex melt-viscosity [η*] of ~10^4-10^5 poise are developed for laser sintering by modifying the original formulation for resin transfer molding (RTM) with [η*] of 30 poise at 280 °C. The RTM385-SLS resin was dry blended with 20-25% h-BN platelets in a ball mill. The h-BN filled resin powder was then subjected to laser sintering, using a laser at 25-38 Watts of power and a powder bed temperature of 180 °C. The filled h-BN platelets apparently impart not only the stiffness, but also a higher heat transfer efficiency (better laser absorptivity due to their higher thermal conductivity) that enables building thicker layers in the LS process, relative to the neat resin as an insulator. However, the "green" h-BN dogbone specimens are very fragile especially near the neckline as some of dogbones broke off while being taken out of the powder bed. These results indicated the laser only promoted sparsely crosslinking of PEPA endcaps. Fortunately, after post-cured at 343 °C (650 °F) for 16 hours, the h-BN composites dogbone specimens greatly improved their strength when all the remaining reactive PEPA endcaps were fully crosslinked to form a network to afford a very high glass transition temperature (T_g) of 395°C. SEM confirmed the h-BN appeared to blend with RTM38-SLS homogeneously and the h-BN platelets were also shown to be exfoliated in the fractured surface of the h-BN composite dogbones, which is impressive. The thermal conductivity of the 25% h-BN/RTM385-SLS composite is ~0.7 W/m.K versus the neat resin of ~ 0.2W/m.K. The porosity of these composite LS-specimens are about ~6-7%, which are considered very good in AM. However, the tensile strength of these h-BN containing LS-dogbones exhibited only about half of the tensile strength of the carbon fiber-filled LS dogbones, due to more flexible carbon fibers with higher aspect ratio that yielded strength as opposed to the rigid ceramic h-BN platelets which embrittled the resultant composites.

In essence, a subscale composite bracket has been successfully manufactured by laser sintering, using carbon fiber filled RTM370 resin powder. A mixture of RTM385-SLS thermoset polyimide resin powder and h-BN platelets has been successfully 3D-printed into composite dogbone specimens that exhibit reasonable thermal conductivity but electrically insulating for use in thermal management for electrified aircrafts and other aerospace applications.

6. ACKNOWLEGEMENTS

The authors would like to acknowledge the funding support from Air Force Research Labs at Wright-Patterson Air Force Base in Dayton, OH for sponsoring the laser sintering of carbon fiber filled RTM370 imide resin project. Additionally, we also like to acknowledge the funding support from NASA Advanced Air Transport Technology (AATT) and Transformational Tools and Technologies (TTT) programs for the laser sintering of h-BN filled RTM385-SLS composite work. Furthermore, we like to thank Daniel A. Scheiman and Linda Mccorkle of Universities Space Research Association for performing thermal analysis, thermal conductivity measurement as well as SEM and rheology. William L. Brown of HX5 Sierra company for conducting mechanical testing on h-BN composite specimens. Moreover, the team effort from University of Dayton Research Institute (UDRI), including Thao Gibson's contribution in cure characterization, Andrew

Abbott and Ron Trejo's help in mechanical testing on carbon fiber composite specimens and Marlene Houtz's X-ray CT are greatly appreciated.

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