Laser Sintering of Thermoset Polyimide Composites

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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 CAD model. SLS 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. Our previous effort showed the challenges of printing a melt-processable RTM370 imide resin powder terminated with reactive 4-phenylethynylphthalic anhydride by LS, due to its inherently low viscosity of these oligomers. This paper presented the first successful 3D printing of high temperature carbon fiber filled thermoset polyimide composites, followed by post cure cycles to promote additional crosslinking for achieving higher temperature (T_g = 370 °C) capability. The processes to build tensile specimens and a component by LS, and the characterization of RTM370 imide resin by DSC and rheology as well as evaluation of the LS printed polyimide composite specimens by SEM and mechanical tests will be discussed.

1. INTRODUCTION

Selective laser sintering (SLS) is an additive manufacturing technique that builds 3D models by using a laser to selectively melt cross section in powdered polymeric materials layer by layer, following the slice of each computer-aided design (CAD) scan. The most commonly used polymers for SLS are polyamides 11 and 12 powders with use temperature ranged from 150-185 °C [1-2]. Recently semi-crystalline PEEK of varied LS-grade powders, with melting temperature (T_m) of 343-370 °C, have 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 compared to traditionally processed materials, due to the lack of polymer inter-chain connection in the z-direction. There are attempts to process epoxy resin by SLS [5] or impregnating liquid epoxy into a green parts built by SLS using polyamide mixed with carbon fiber [6]. However, the real incentive of developing a SLS process for thermoset resins lies in the potential of raising use temperature to 250-300 °C for 3D-printed objects, and the prospect of printing polymer carbon fiber composites for aerospace applications. Previously we reported the challenges of attempting to print a melt-processable RTM370 imide resin powder terminated with reactive phenylethynyl (PEPA) groups into thermoset polyimides by LS [7].

As described in the previous article, we realized the viscosity of resin designed originally for resin transfer molding (RTM) was too low, and the laser apparently only melted the resin without curing the reactive PEPA endcap. As a result, the LS-printed resin chips could not hold much integrity upon postcure above 250 °C. To overcome the low viscosity of the resin, the standard RTM370 resin was further staged for 2-4 hours at 300 °C to promote chain extension while still maintaining melt-proccessability and avoiding extensive crosslinking of PEPA endcap.

2. EXPERIMENTATION

Standard RTM370 resin produced by Imitec Inc. was further staged for 2-4 hours at 300 °C to promote chain extension while avoiding extensive crosslinking of the PEPA endcaps for use in LS. Short carbon fibers (length ~60μ) was obtained from Advanced Laser Materials, LLC (now part of EOS North America). Carbon fiber (35 wt%) was added to the RTM370 resin further staged at 300 °C for 3 hrs, and then dry blended in a rotating drum tumbler to ensure a consistent blend. To save the materials used for this LS study, SinterStation 2500 was retrofit with a small 10 × 10 cm build chamber (Fig. 1) 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 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. The differential scanning calorimetry (DSC) was conducted on TA Instruments Q1000 with 5 °C/ min. heating rate. The thermal conductivity was measured on C-Therm TCi thermal conductivity analyzer. AccPyc II Pycnometer by Micromeritics was used to measured porosity in LS disk.

Figure 1. A small build chamber in a build piston

3. RESULTS AND DISCUSSION

3.1 Laser Sintering of RTM 370 Resin:

Our previous attempt to produce durable resin chips by LS using "as received" RTM370 powder indicated that its viscosity (~30 poise) was too low for LS, because it was originally designed for resin transfer molding (RTM) application. Therefore, RTM370 resin was further staged at 300 °C for 2.5 hours to afford a resin with higher viscosity, indicative of higher chain extension as evidenced by the formation of a filaments inside the rheometer (Fig. 2). DSC thermogram showed a T_g of ~170 °C and a PEPA endcap curing at 372 °C (Fig. 3).

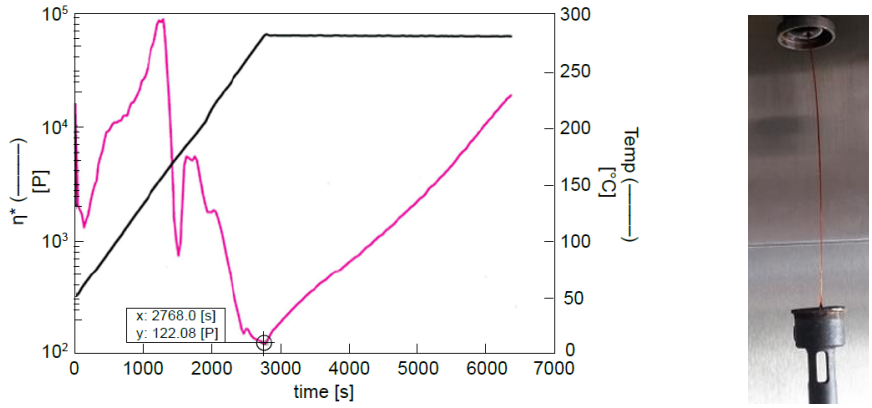


Fig. 2. Viscosity of RTM370 resin staged at 300°C for 2.5 h and the filament formation

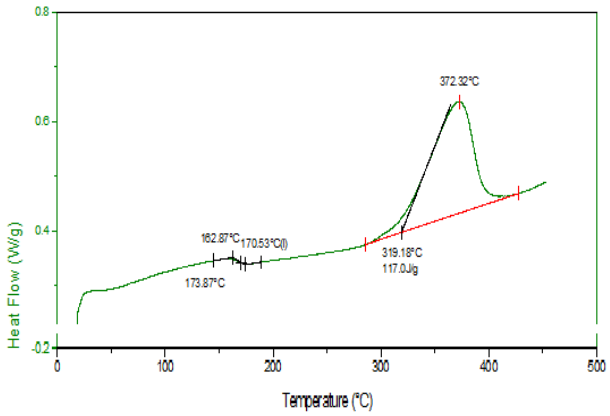


Figure 3. DSC of RTM370 resin after staging at 300 °C for 2.5 h

Using parameter listed in Table 1, several sets of 6 resin chips (1-6 scans) were produced by LS using further staged RTM370 resin, and they appeared very uniform (Fig. 4). However, when warming to 200 °C in an oven, the resin chips appeared to soften. Then the chips started to melt and loose integrity when reaching 250 °C, indicating that the PEPA endcaps probably have not been fully cured.

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)

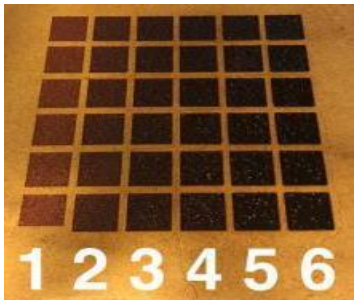


Figure 4. LS printed resin chips

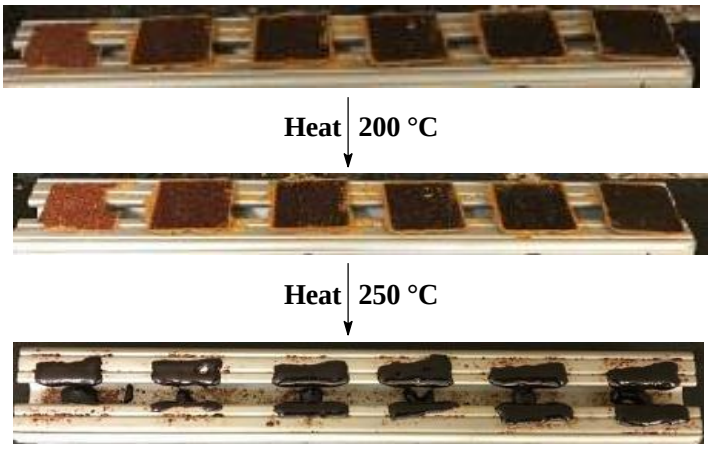


Figure 5. Resin chips with multiple scans subjected to postcure in an oven

3.2 Laser Sintering of RTM 370 /Carbon Fiber Composites:

To improve the stiffness of the build layers, RTM370 resin was mixed with 35% carbon fibers (~60 µl 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. 5) than any of the neat resin with or without further staging at 300 °C in previous LS runs. It is believed that the filled 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 of laser. The depth of penetration (chip thickness) also increased with increasing number of scans, although DSC thermogram still showed significant exotherm of the uncured PEPA endcap at 370 °C, indicating that the green composite disks are not fully cured yet. The thermal conductivity of the carbon fiber-filled RTM370 LS disk in Fig. 6 (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 5. Carbon-fiber-filled RTM370 composite chips by LS

Figure 6. Carbon-fiber-filled LS-printed disk (left) and neat resin disk (right)

3.3 Laser Sintering of Composite Specimens:

I) <u>100 µm Thickness Layers</u>: With the success of producing the single scan composite chips 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 instead was "bulldozing". Due to the change in the location of the thermocouple to control the feed temperature, it was thought that the powder may be overheating. 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 to high is the feed bed "cracking" shown in Fig. 7.

Figure 7. Composite feed bed cracking due to high heat

A number of 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. This shifting is shown below during the build and post build (Fig. 8).

Figure 8. Layers shifting during the build and post building

II) <u>125µm Thickness Layers</u>: To build thicker layer, 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 but 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. 9). The part then "rocks" as the roller/spreader assembly moves across the part bed.

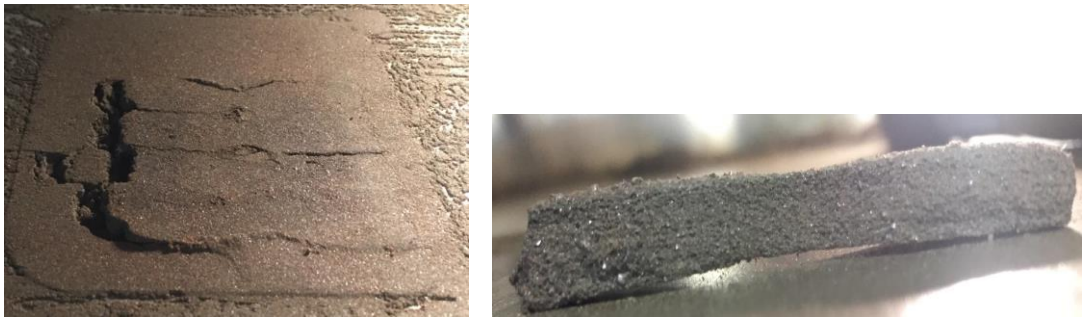


Figure 9. Warping during the build and sample curling post building

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 of the metal parts to come to equilibrium and heat soak in an attempt to minimize curling. While the curling was starting to be much less visible, there was still layer shifting occurring.

<u>III) 150 µm Thick Layers</u>: 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 consistent feed temperature control. However, a number of subscale tensile specimens (Fig. 10) for postcure and mechanical tests were successfully 3D printed, besides a few round disks (25 mm diameter × 2 mm thick) and 0.6 cm cubes printed for characterization, using the parameters listed in Table V.

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 10. Tensile specimens during LS build process and after post build

IV) 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. 11), relative 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. 12). These are likely due to agglomeration of resin particles after additional staging/heating as well as carbon fiber 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.

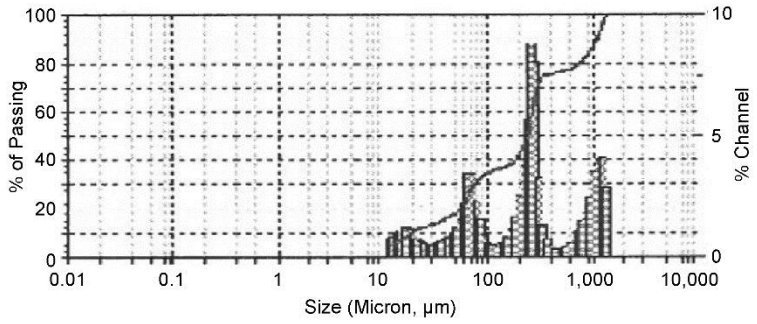


Figure 11. Particle size distribution of further staged RTM370 blended with milled carbon fiber

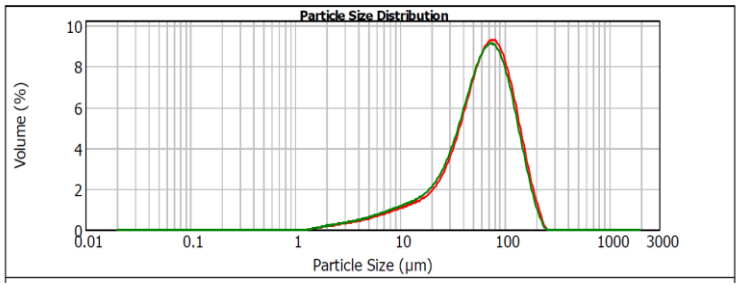


Figure 12. Original particle distribution of RTM370 for RTM process

3.4 Characterization of LS-Printed Tensile Specimens:

Half a dozen dogbones subscale specimens [6.5cm × 0.9 cm × 0.5cm 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 in order to complete total cure of PEPA endcaps and achieve optimal mechanical properties. 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 as shown in Fig.13a-c and SEM micrograph of the fractured LS-printed composite (Fig. 14) 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 19 °C.

a) Gauge Fracture b) Fracture Surface c) Angled

Figure 13. Fracture surfaces of dogbone subscale tensile specimens

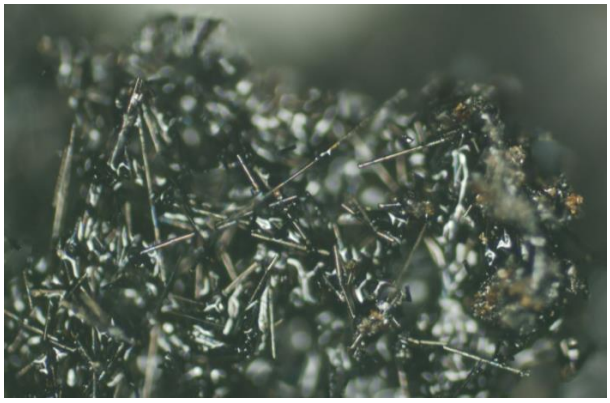


Figure 14. SEM micrograph showed milled carbon fibers at fracture surface

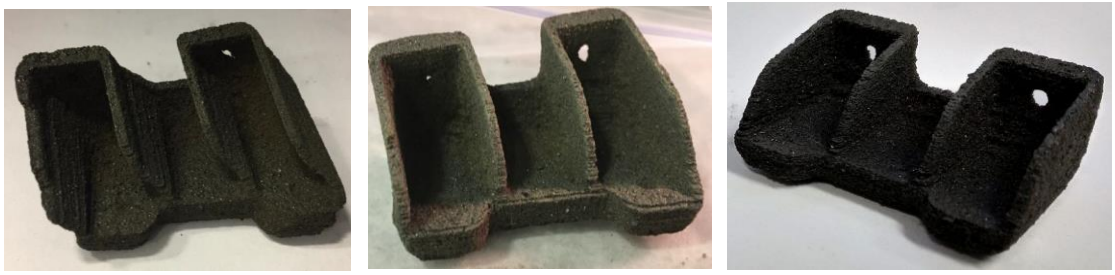
Table 6. Tensile Property of LS-Printed Specimens

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**

1) Test rate: 0.127 cm/min (0.5 in/min); Grip pressure: 1.38 MPa (200 psi)
2) Furnace temperature equilibrated and specimens conditioned 15 min before testing
3) 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. 15A). Using longer heat soak times helped somewhat, but not until there was full thermal control in piston and cylinder heater temperature control as well as the overhead part bed heating (Fig. 15 B). Eventually, the 30% scaled geometric bracket was built well as a successful 3D components by LS (Fig. 15C). 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 manufacture field that can be used for >300 °C aerospace applications.



A B C

Figure 15. Stages of composite brackets printed by LS

4. CONCLUSION

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 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 polyimide composites with glass transition

temperature (T_g) of 370 °C printed by LS. Another advantage of this major 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. In essence, this research ushers in the new era of using additive manufacturing to produce high temperature thermoset polyimide composite parts for >300 °C applications.

5. ACKNOWLEGEMENTS

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