

Laser Sintering of RTM385-SLS Thermoset Polyimide with Boron Nitride

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ABSTRACT

RTM385-SLS is a melt-processable thermoset polyimide resin specially formulated with a complex melt viscosity (η^*) of $\sim 10^4$ - 10^5 poise for laser sintering. RTM385-SLS resin powder was mixed with 20-25% of hexagonal boron nitride (h-BN) and subjected to laser sintering (LS) to print out “Green” disks and dogbone specimens which could be further post-cured in an oven to complete the crosslinking of the reactive phenylethynylphthalic anhydride (PEPA) terminal groups within the resin to achieve a very high glass transition temperature (T_g) of 385°C. The cured composite specimens were then subjected to thermal analysis, thermal conductivity measurement and mechanical testing for characterization.

1. INTRODUCTION

Selective laser sintering (SLS) is an additive manufacturing (AM) technique that builds 3D models by using a laser to selectively melt cross sections in a bed of powdered polymeric materials layer by layer, following the slices of each computer-aided design (CAD) file (Fig. 1a). The commonly used polymers for SLS are polyamides 11 and 12 powders with use temperature ranging from 150-185°C [1-2]. Recently semi-crystalline PEEK of varied LS-grade powders with a melting temperature (T_m) of 343-370°C, were heated up to 380°C to be manufactured into 3D objects by a more elaborate high temperature laser sintering (HT-LS) machine and process, affording PEEK components with a 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 their inherent higher porosity generated by AM processing and the lack of polymer inter-chain connection in the z-direction. Therefore, it is essential to develop laser sintering processes for thermoset polymers with 250-300°C use capability for aerospace applications. Recently a thermoset bismaleimide resin was blended with thermally conductive carbon micro-balloons to increase its laser absorbability for a successful laser sintering [5].

Initially we have attempted to print a melt-processable RTM370 thermoset polyimide oligomer powder terminated with reactive phenylethynylphthalic (PEPA) endcaps by laser sintering into 3D objects [6], but soon realized the viscosity of the material originally developed for resin transfer molding (RTM) was too low, and the laser seemed only melted the resin without curing the reactive PEPA endcap, leading to specimens with voids. To overcome the low viscosity of the resin, the standard RTM370 resin was further heated at 300°C for 2-3 hours to increase the viscosity by promoting chain extension while still maintaining melt-processability, thus avoiding extensive crosslinking of the reactive PEPA endcaps within the resin. The further staged RTM370 was able to 3D print specimens with integrity by LS (Fig.1b).

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Previously when RTM370 resin was filled with finely milled carbon fibers, the thermal conductivity of carbon fibers enhanced the efficiency of the laser sintering to 3D print dogbone specimens (Fig.1c) due to better energy absorption. Eventually a high temperature RTM370 thermoset polyimide/carbon fiber composite bracket with >300°C capability (Fig. 1d) was additively manufactured by laser sintering for the first time [7].



Figure 1. Laser sintering of RTM370 thermoset polyimide resin and composites

Based on the lesson learned from the laser sintering of RTM370 resin (cured $T_g = 370^\circ\text{C}$), RTM385-SLS resin (cured $T_g = 385^\circ\text{C}$) was specially formulated to display a complex melt-viscosity (η^*) of about 5×10^4 poise suitable for laser sintering as received. In this project, 20-25wt% of h-BN was mixed with RTM385-SLS using a ball mill and then laser sintered.

2. EXPERIMENTATION

The RTM385-SLS for laser sintering was manufactured by Imitec Inc. The hexagonal boron nitride platelets (30 μm , 98.5% pure) were purchased from American Elements. The RTM385-SLS resin and h-BN were dry blended by ball milling to achieve a homogeneous powder mixture. To save the material for this LS study, the DTM SinterStation 2500 Plus SLS 3D printer was retrofitted with a smaller 10 cm $\times$ 10 cm build chamber (Fig. 2) out of the original build piston. Both the build piston/cylinder and the feed cartridges had to be modified to accommodate the smaller build chamber. The temperature of the part bed is monitored and controlled by an infrared sensor. The temperature of the feed cartridge is also measured using a thermocouple. The rheology of the resin was performed in the parallel plate geometry with 1g of imidized powder at a ramping rate of 4 $^\circ\text{C}/\text{min}$ and frequency at 10 rad/sec, using an Ares Rheometer. The differential scanning calorimetry (DSC) was conducted on TA Instruments Q1000 with 5 $^\circ\text{C}/\text{min}$ heating rate. The thermal conductivities were determined by modified transient plane source (MTPS) method on C-Therm TCi thermal conductivity analyzer. The porosity of the LS specimens was measured by AccPyc II Pycnometer by Micromeritics.

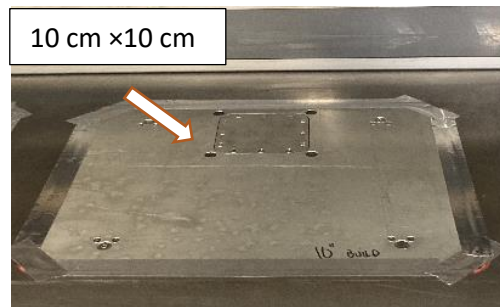


Figure 2. A small build chamber (10'' $\times$ 10'')

3. RESULTS AND DISCUSSION

3.1 Laser sintering of RTM385-SLS neat resin

The rheology of RTM385-SLS oligomer powder shown in Figure 3 indicating the complex melt-viscosity (η^*) is holding steady at $\sim 50,000$ poise at 280°C for 1-2 hours (Fig. 3). 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. 4), because the reactive PEPA endcaps within the resin are not fully cured yet during the LS process.

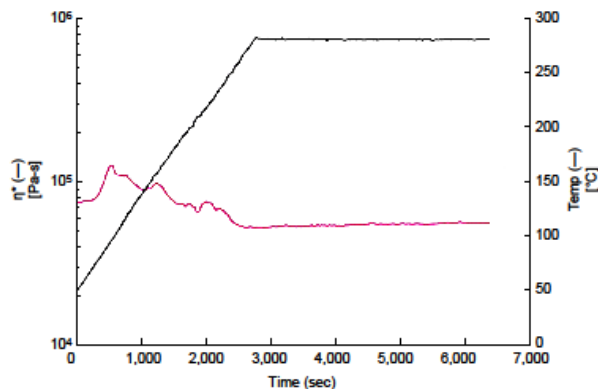


Figure 3. Rheology of RTM385-SLS imide oligomer powder

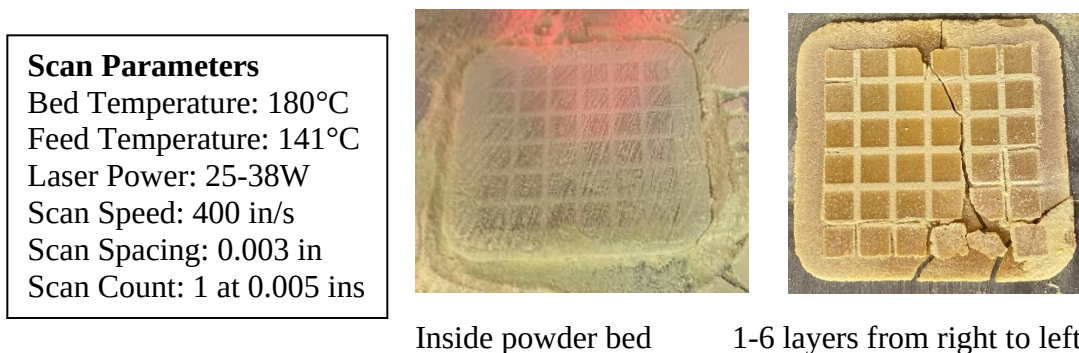


Figure 4. Laser sintering of RTM385-SLS oligomer powder

3.2 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 with h-BN. 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 5A). 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 5B). 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 5C). 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 high volume of h-BN at 30wt% ratio of h-BN with resin is too high to bond 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 ins

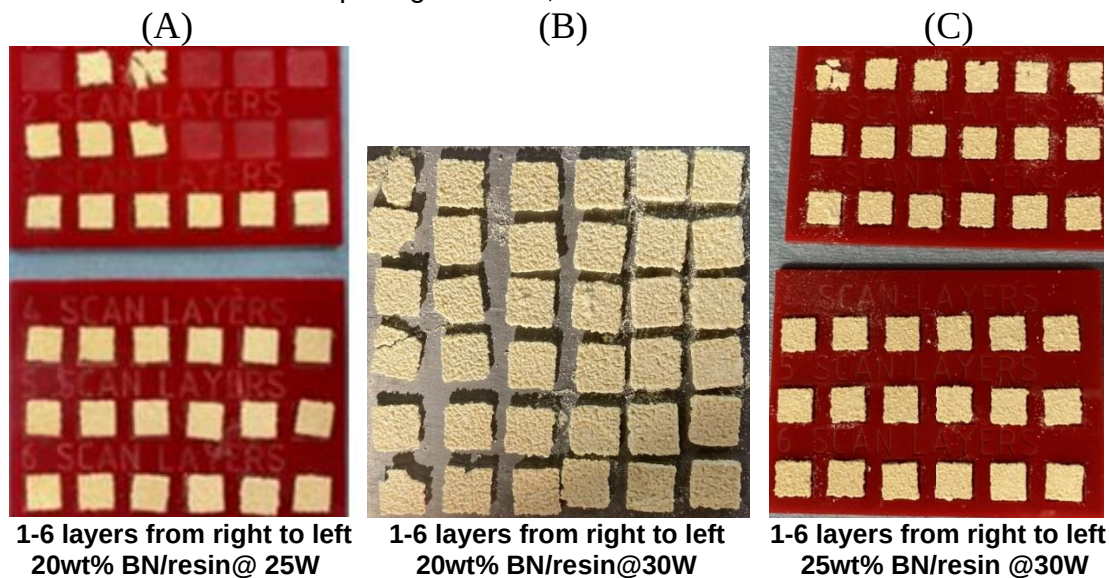


Figure 5. Laser sintering of BN/RTM385-SLS composite disks

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. 6 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 endcap was only sparsely cured by laser. The lack of PEPA crosslinking in resin to build a 3D network is the reason why the green h-BN composite dogbones are so fragile.

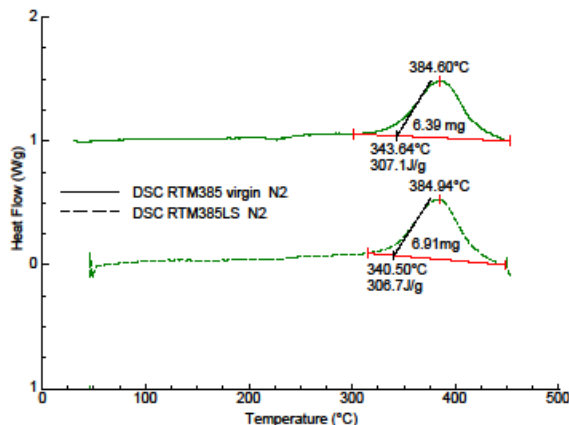


Figure 6. DSC thermograms of PEPA endcaps curing of RTM385 virgin vs RTM385-LS

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. 7A. When the power was increased to 35W, the strength of the dogbone specimens improved with 25wt%BN/resin with only 1 out of 4 broken necks and the texture appeared more consolidated, although these “green” specimens are only partially cured (Fig. 7B). At 38W, 25wt% BN, about 1 out of 5 dogbones resulted in broken neck (Fig. 7C), but the 38W power sometimes had a tendency of over-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 laser (Fig. 7D). Also, it seemed that the h-BN filler is more brittle than the milled carbon fibers which have a higher aspect ratio that offers entanglement to strengthen the composites in prior study (7).

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 ins

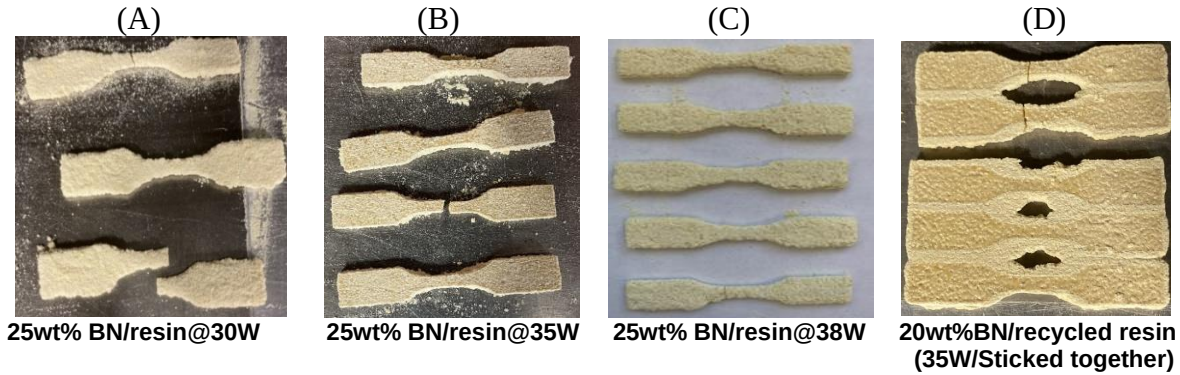


Figure 7. Laser sintering of BN/RTM385-SLS composite dogbone specimens

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

The as-sintered h-BN composite dogbone specimens in Fig. 7 (B-C) are post-cured in a blue M oven as follows: a) Ramped from room temperature to 232°C (450°F) in 2 hrs and then hold at 232° for 2 hrs. b) Ramped from 232°C to 243°C (650°F) over 8 hrs and hold at 243°C for 16 hrs and then cooled. The post-cured dogbones specimens are shown in Figure 8 and 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 the neat resin of ~ 0.2W/m.K. 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. 8) shows that h-BN platelets are evenly distributed throughout the LS-printed samples.

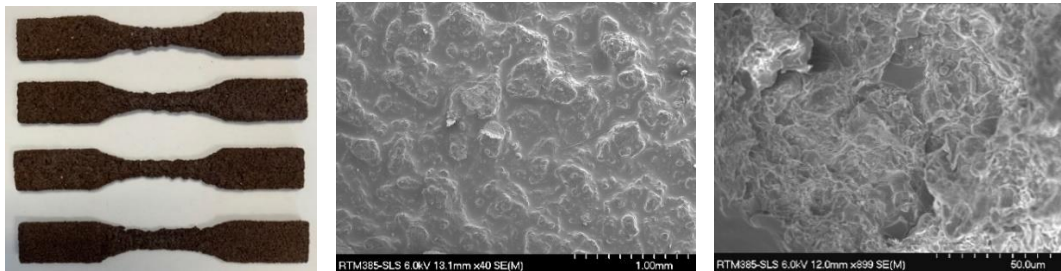


Figure 8. Photo and SEM of cured h-BN/RTM385-SLS composite dogbone surface

3.4 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 nitride 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 1, 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. However, the tensile strength of these BN containing LS-dogbones only exhibited about half of the strength compared to the carbon fiber-filled LS dogbones presented in a previously reported article [7]. 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 micrograph (Fig. 9) 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 1. 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) Instu-Met 4505, 90/22 with 100KN capacity was used.

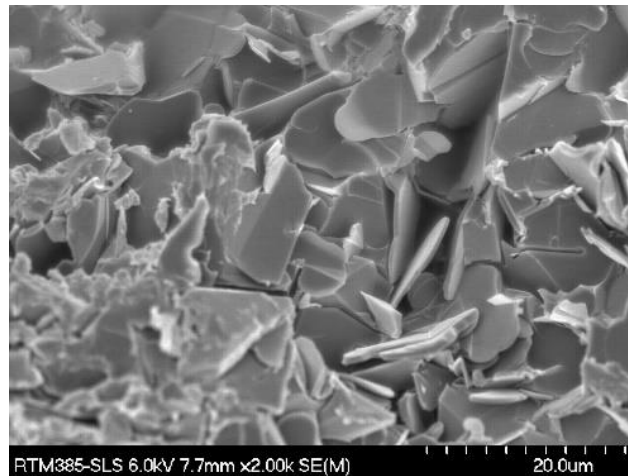


Figure 9. SEM micrograph of fracture surface of exfoliated h-BN platelets

4. CONCLUSION

This laser sintering project is a continue investigation of using melt-processable thermoset RTM polyimide resins for additive manufacturing. The major goal is to design a new melt-processable resin, namely RTM385-SLS with a complex melt-viscosity (η^*) of $\sim 10^4$ - 10^5 poise, which is more suitable for laser sintering than the inherently low melt-viscosity (10-30 poise) exhibits by RTM370 resin that was originally designed for resin transfer molding (RTM) application. 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, relative to the neat resin as an insulator in the LS process. 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 as compared to previously reported samples filled with milled carbon fibers that offer higher aspect ratio for entanglement to exhibit better strength. These results indicate 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 into 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. The thermal conductivity of the 25% h-BN/RTM385-SLS composite is ~ 0.7 W/m.K versus the neat resin of ~ 0.2 W/m.K. The porosity of these composite LS-specimens is about ~ 6 -7%, which are considered very good in AM.

In essence, a new high temperature RTM385-SLS thermoset polyimide resin with a T_g of 385°C and a complex melt-viscosity (η^*) of $\sim 10^4$ - 10^5 poise that is suitable for laser sintering has been developed. Mixture of RTM385-SLS thermoset polyimide resin powder and h-BN platelets have been successfully 3D-printed into composite dogbone specimens that exhibit reasonable thermal conductivity and mechanical strength for use in thermal management for potential aerospace applications.

5. ACKNOWLEDGEMENTS

The authors would like to acknowledge the funding support from NASA Advanced Air Transport Technology (AATT) and Transformational Tools and Technologies (TTT) programs. Also, the authors like to thank Mr. William L. Brown of HX5 Sierra company for conducting mechanical testing of additively manufactured composite specimens.

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