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Additive Manufacturing Research Group

Laser Sintering of RTM385-SLS Thermoset Polyimide with Boron Nitride

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Polymer Laser Sintering

- **<u>Laser Sintering</u> (LS) builds 3D models layer by layer using a laser to selectively melt cross sections in powdered polymers**
  - Traditionally, LS are conducted with thermoplastic resins, such as Polyamides (e.g. Nylon 12), or more recently PEEK (melted@380°C with 250°C use temp.)
  - Previously demonstrated feasibility of LS using RTM370 thermoset imide resin filled with finely-milled carbon fibers to print a composite bracket (CAMX2019)







Laser Sintering of Thermoset Polyimide Composites with h-BN

♦ **Goal: To conduct LS of thermoset imide resins filled with Boron Nitride (BN) to 3D-print thermally conductive, but electrically insulating high temperature thermoset polyimide composites with > 300°C capability for aerospace use**

♦ **Candidate: New RTM385-SLS thermoset imide resin made by a solvent-free melt process ⇒ ready for laser sintering as received**

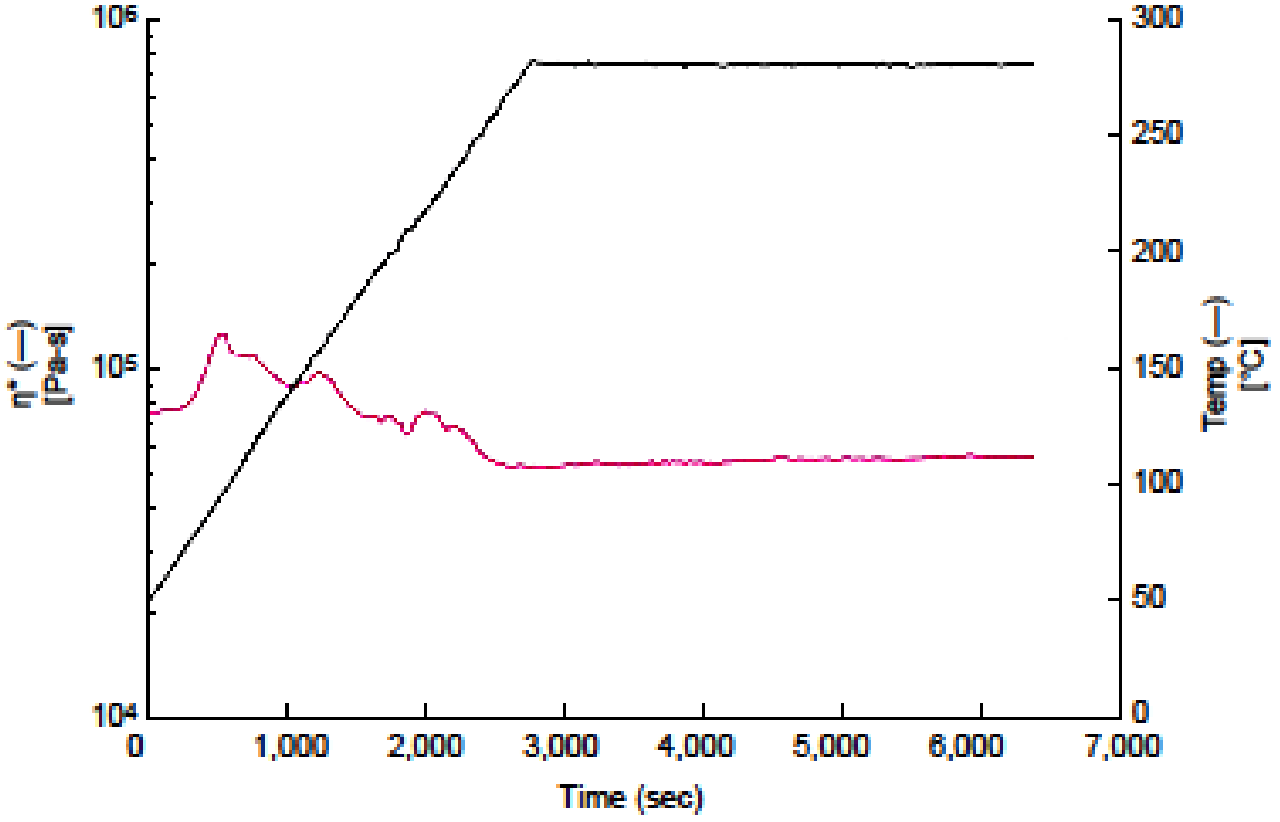
♦ **Lesson Learned:**

- **Standard RTM370 imide resin, [η*] =30 poise at 280°C which flows too much for LS process ⇒ Creating spider webbing & voids in specimens**
- **Remedy: To limit resin flow by increasing resin viscosity via further heating**

  RTM370 at 300°C for 2-3 hrs to promote chain extension, but not much of crosslinking

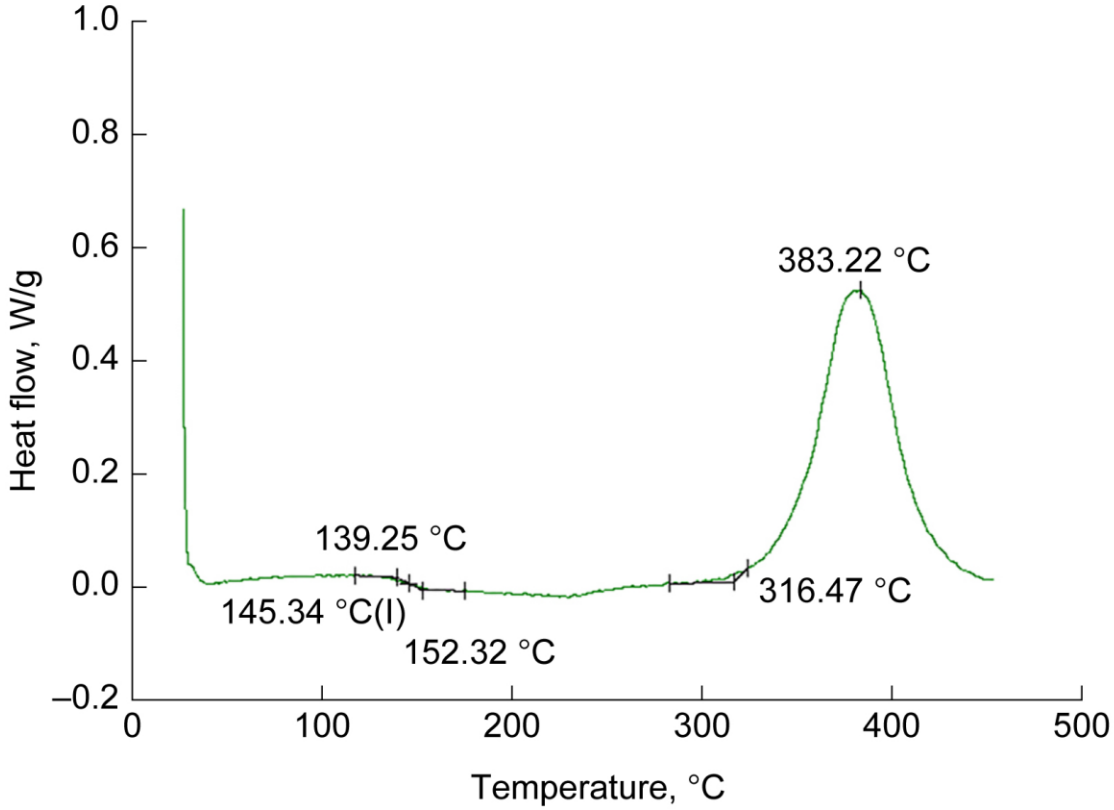
⇒ Developed new RTM385-SLS formulation, [η*] = 50,000 poise at 280°C for LS

RTM385-SLS Resin Properties suitable for LS



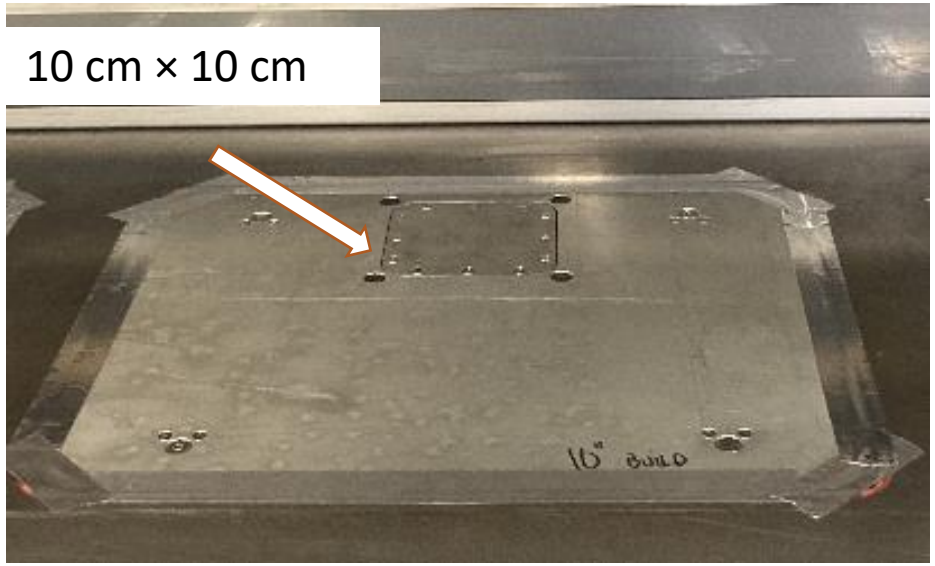
Rheology of RTM385-SLS

Complex viscosity [η*] ~5 × 10^4 poise at 280°C



DSC thermogram of RTM385-SLS

Modified SinterStation 2500

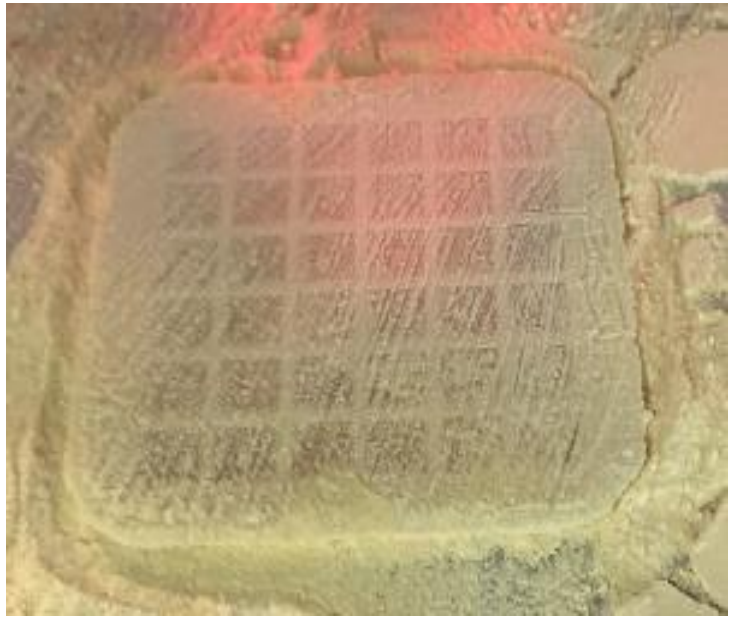


A build chamber of 10” by 10”

- SinterStation 2500 was retrofit with a small 10 cm × 10 cm build chamber out of 10” by 10” chamber ⇒ to save materials
- Part bed is monitored and controlled by an infrared sensor
- The temperature of feed cartridge is monitored by a thermocouple
- Use CO_2 laser of 10.6 micron wavelength

Laser sintering of RTM385-SLS 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



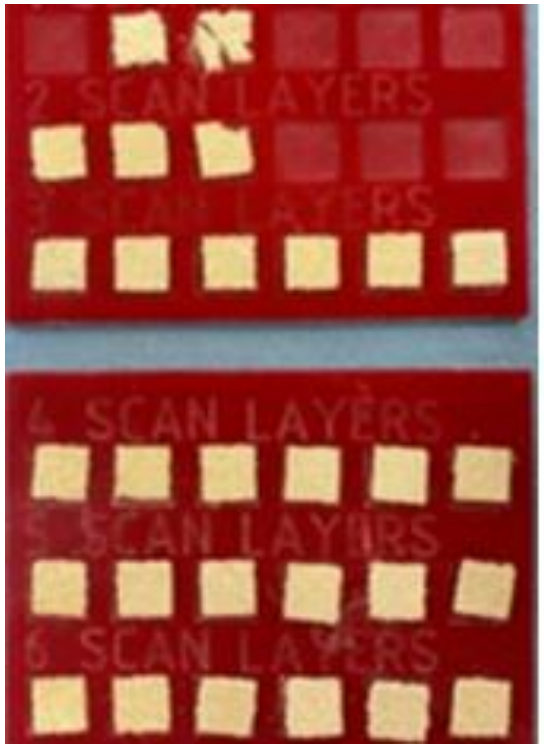


- **The LS-Printed square resin disks are caked together and fragile**
- **Nevertheless, it shows that RTM385-SLS can be laser sintered as received**

Laser Sintering of RTM385-SLS with Hexagonal Boron Nitride (25wt% h-BN)

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

(A)



1-6 layers from top to bottom
20wt% BN/resin@ 25W

(B)



1-6 layers from top to bottom
20wt% BN/resin@30W

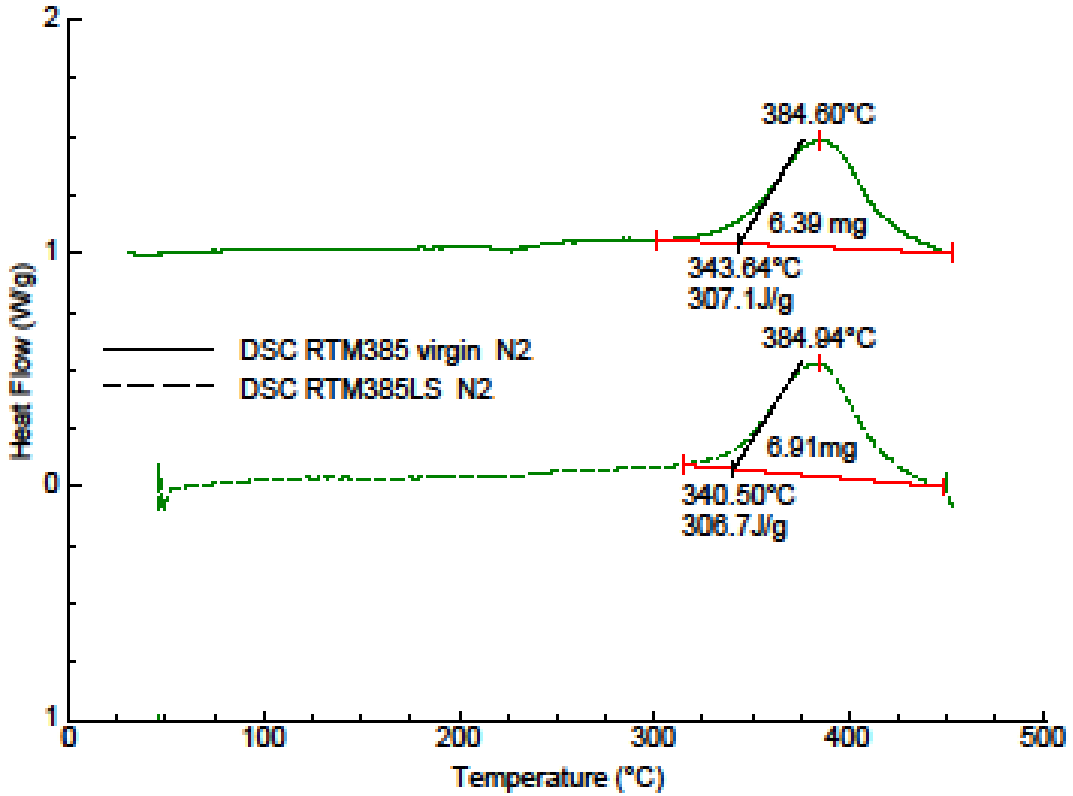
(C)



1-6 layers from top to bottom
25wt% BN/resin @30W

DSC Analysis of RTM385-SLS Resin

Virgin *vs* Sintered Resin at 30W



- The heat flow difference between virgin resin vs sintered resin is 0.4 J/g (<0.2%)
- Laser only slightly cured RTM385-SLS resin at 30W ⇒ Crumble/brittle resin disk

Laser sintering of BN/RTM385-SLS composite dogbone specimens

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

(A)



25wt% BN/resin@30W

1 out of 3 broken neck

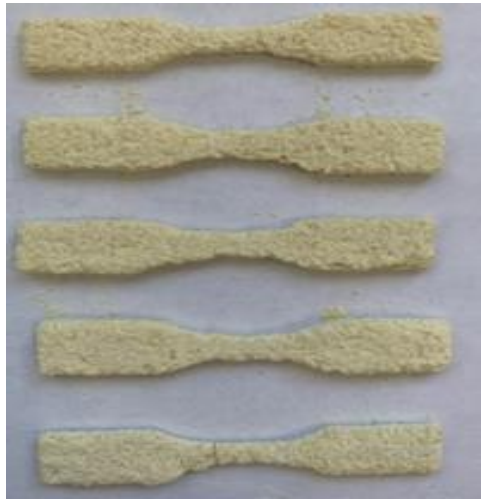
(B)



25wt% BN/resin@35W

1 out of 4 broken neck

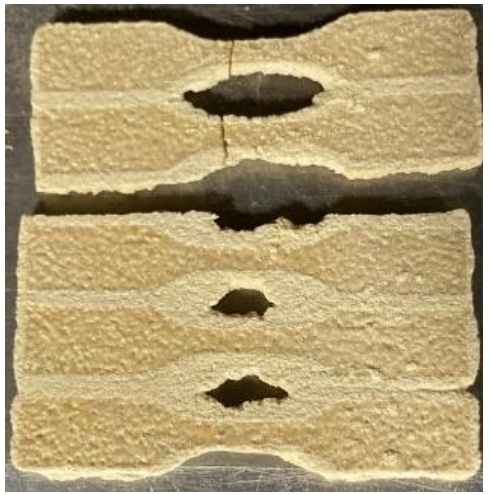
(C)



25wt% BN/resin@38W

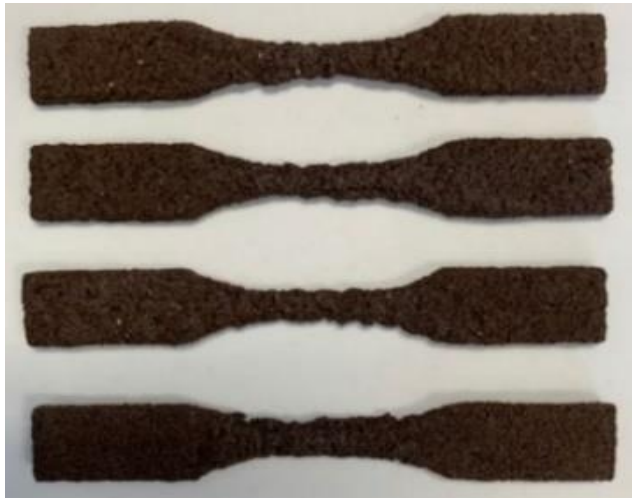
1 out of 5 broken neck (resin over-melt sometimes)

(D)

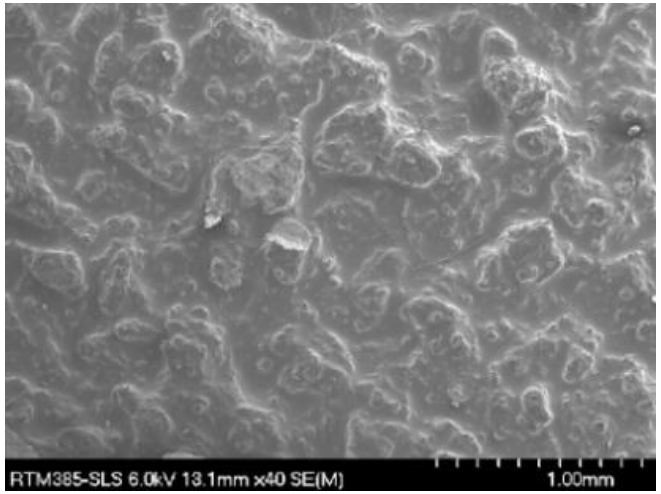


20wt%BN/recycled resin (35W/Sticked together)

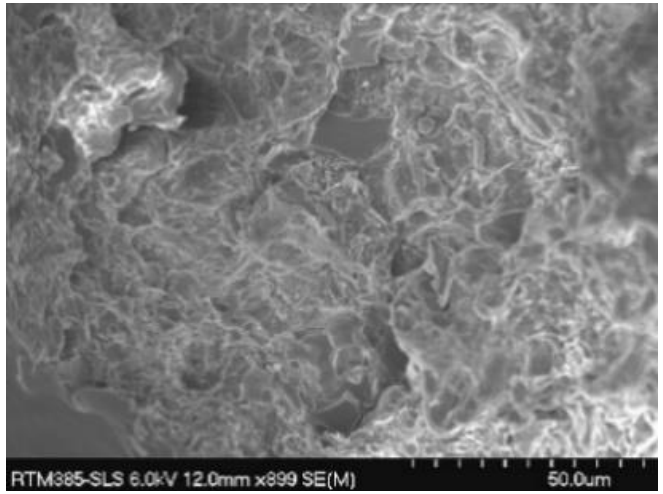
Photo and SEM of Cured h-BN/RTM385-SLS Composite Dogbone Surface



Post-cured@343°C(650°F)/16h
(T_g =395°C)



SEM of dogbone surface reveals h-BN platelets



Enlarged SEM of dogbone surface

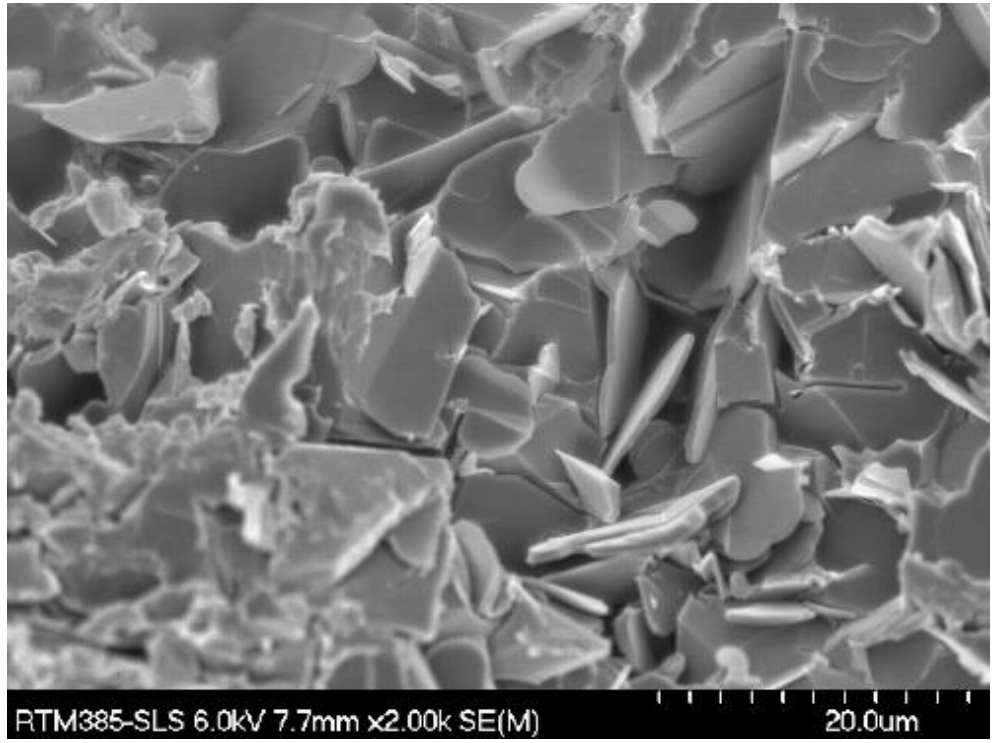
- **The neckline of dogbones show zig zag pattern instead of smooth boundary line**
  ⇒ possiblely contribute to the weak tensile strength
- **SEM reveals that BN platelets are evenly distributed within the resin domain in the LS-printed dogbones**

Characterization of 35W-Printed BN/RTM385-SLS Composite Dogbones

Tensile Property of 35W LS-Printed Specimens[1]

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) The dogbone specimens used in the test is post-cured at 365°C for 16 hrs.
2) Test rate: 0.127 cm/min (0.5 in/min).
3) Vice clamps were used to grip the specimens instead of hydraulic grips.
3) Instru-Met 4505, 90/22 with 100KN capacity was used.



- **Tensile Strength of dogbone specimens (T_g=395°C) at 250°C is comparable to that of ambient**
- **SEM shows h-BN platelets are exfoliated on the fracture surface of the cured LS-printed dogbone**

Conclusion

- Novel RTM385-SLS with [η*] of 5 ×10^4 poise is suitable for laser sintering
- RTM385-SLS filled with thermally conductive h-BN enhances the heat transfer efficiency of the laser ⇒ enabling building thicker layers in the LS process
- 25wt% h-BN/RTM385-SLS was subjected to LS at 25-38W at 180°C bed temp.
- The as-print "Green" dogbones are fragile, especially at the neckline
  ⇒ The laser only sparely cure the reactive PEPA endcaps within the resin
- After 16 hrs of post-cure at 365°C, the dogbone strength greatly improved
  ⇒ All the PEPA endcaps have been fully cured to form crosslinks
- Thermal conductivity of 25wt% BN/RTM385-SLS composites is ~0.7W/m.K (neat resin ~0.2 W/m.K) and the composite porosity is 6-7% (very good for AM)
- SEM shows h-BN platelets are evenly distributed within the resin domain and the dogbone fracture surface reveals that the h-BN are exfoliated
- Tensile strength of h-BN composites is only half of carbon fiber composites
  ⇒ Carbon fibers have higher aspect ratio which offers entanglement to impart composite strength, whereas h-BN platelets contribute to brittleness

Acknowledgements

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