Challenges in Laser Sintering of Thermoset Imide Resin

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Polymer Laser Sintering

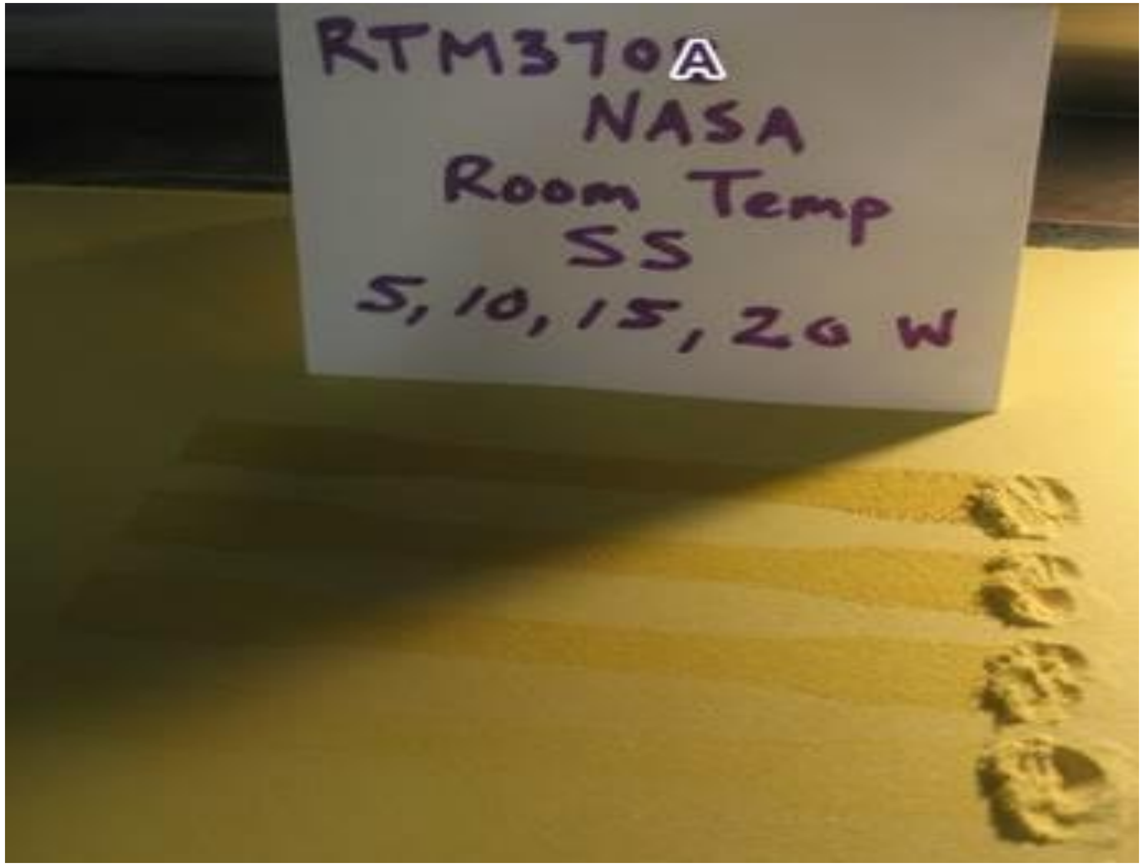
- **<u>Laser Sintering</u> (LS) builds 3D models layer by layer using a laser to selectively melt cross sections in powdered polymers**
  - Traditionally, LS are conducted with thermoplastic resins, such as Polyamides (e.g. Nylon 12), or more recently PEEK

- **<u>Project Goal</u>: To investigate the LS of thermoset resins with a goal to eventually conducting 3D printing of composites with chopped carbon fibers by LS**

- **Candidate: RTM370 thermoset imide resin made by a solvent-free process**
  - **RTM370 resin has been fabricated into composites with excellent mechanical property retention by resin transfer molding (RTM) and resin film infusion (RFI).**

Single scan of laser sintering of RTM370 resin at room temperature

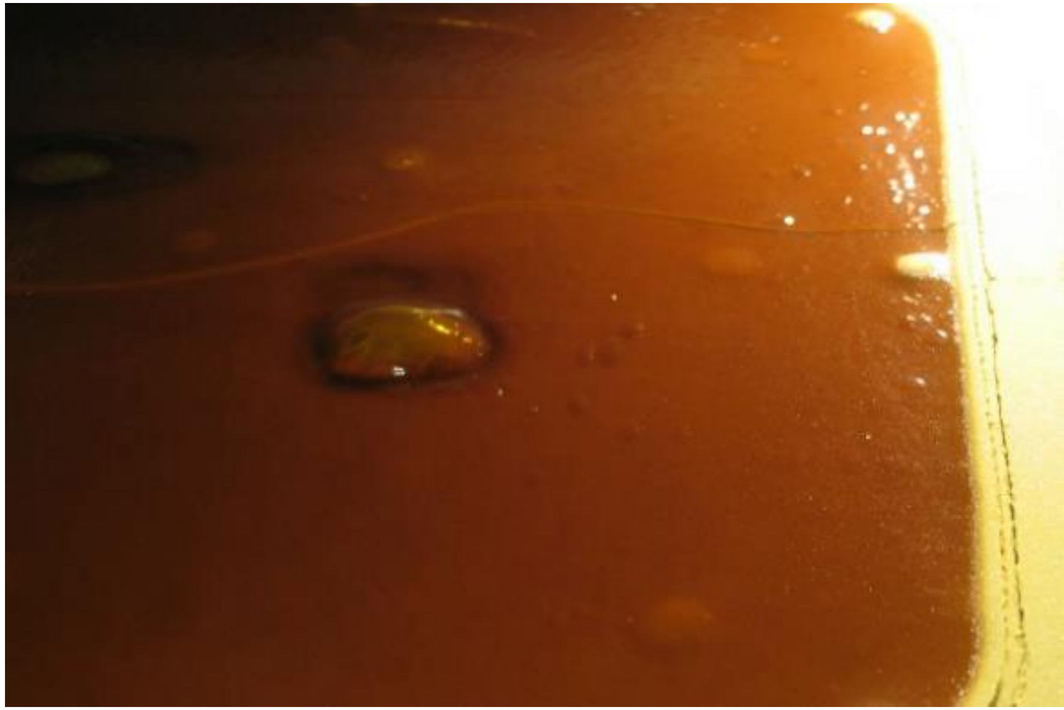
(Scan rate = 508 cm/sec, scan spacing = 0.015 cm)



Insufficient energy to bond the particles into a layer for removal

Material did not melt and flow, but balled

Laser Sintering of RTM370 at 185 °C Bed Temperature



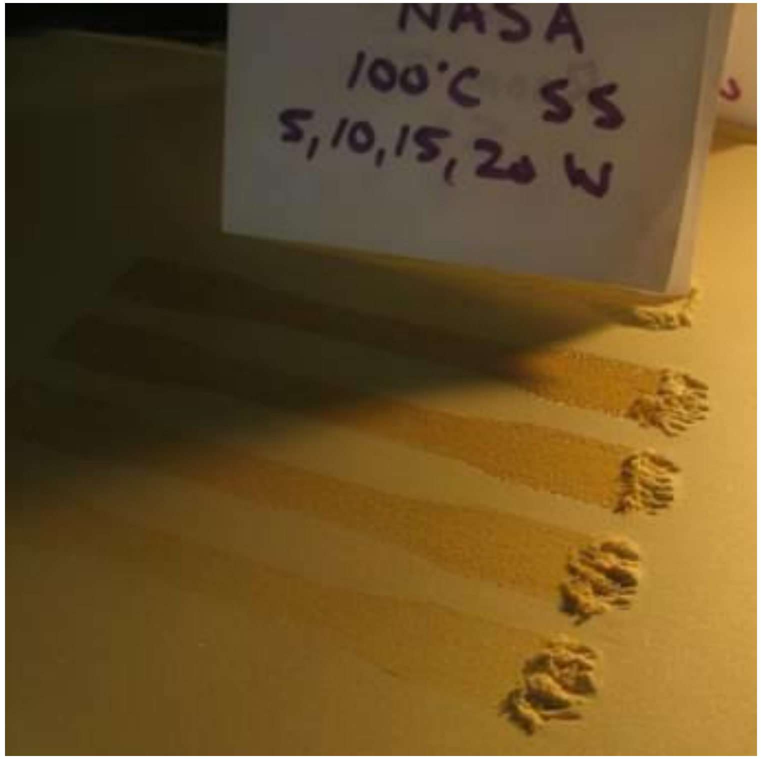
A) Total melting at 185 °C

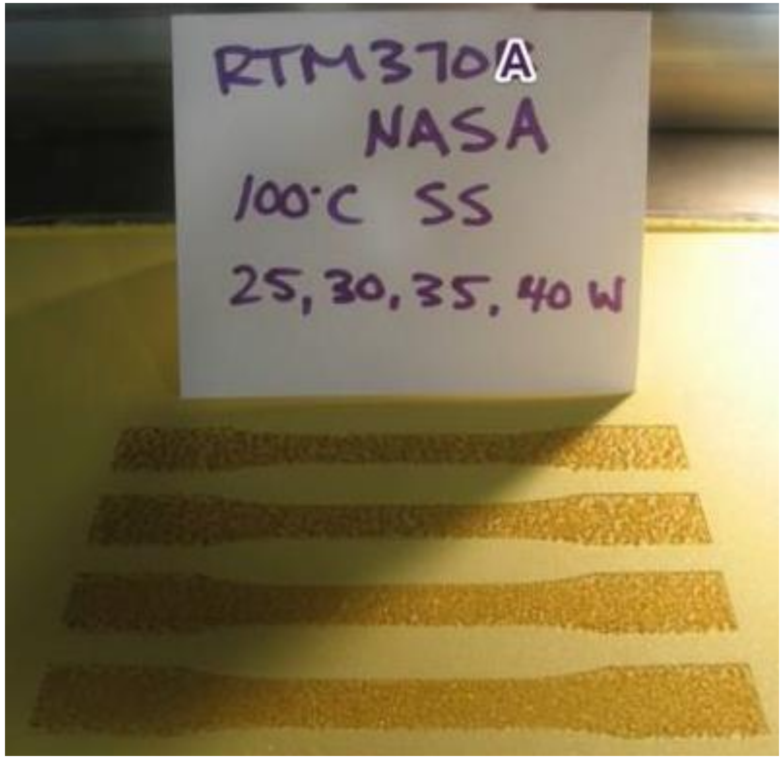
B) Brittle upon removal

- DSC melting endotherm is 150 °C for RTM 370

Single scan of LS at 100 °C

(Scan rate = 508 cm/s, scan spacing = 0.015 cm)





A) 10, 15, 20 Watts

B) 20, 30, 35, 40 W

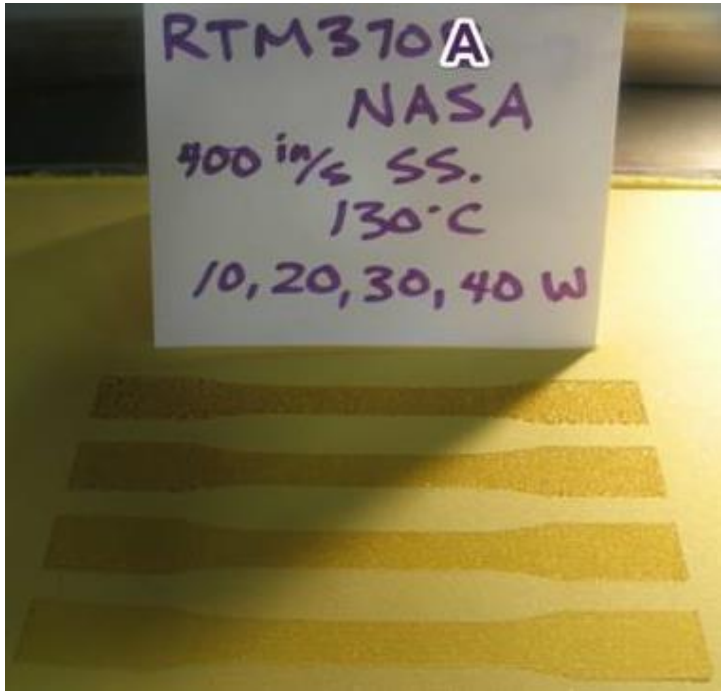
40 35 30 25 W

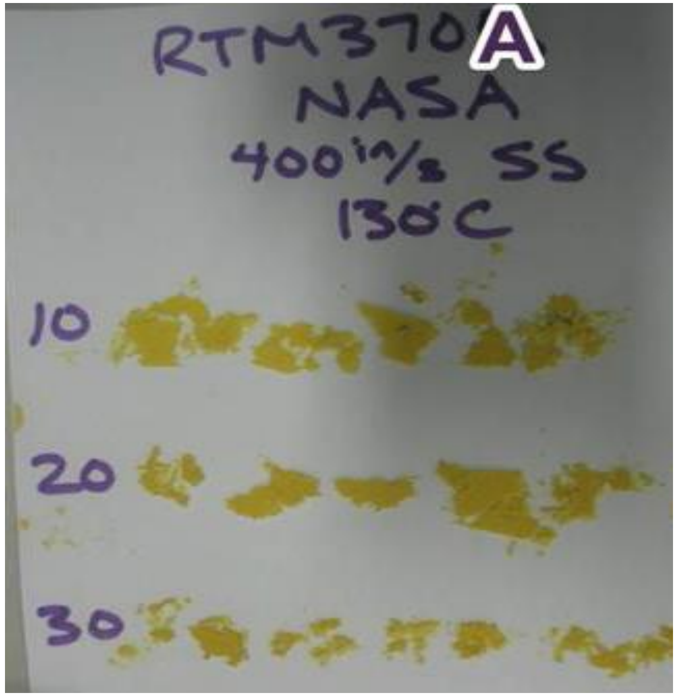
No sufficient energy for agglomeration

Balling was evident at 35 & 40 W but no melt flow

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)





40 30 20 10 W

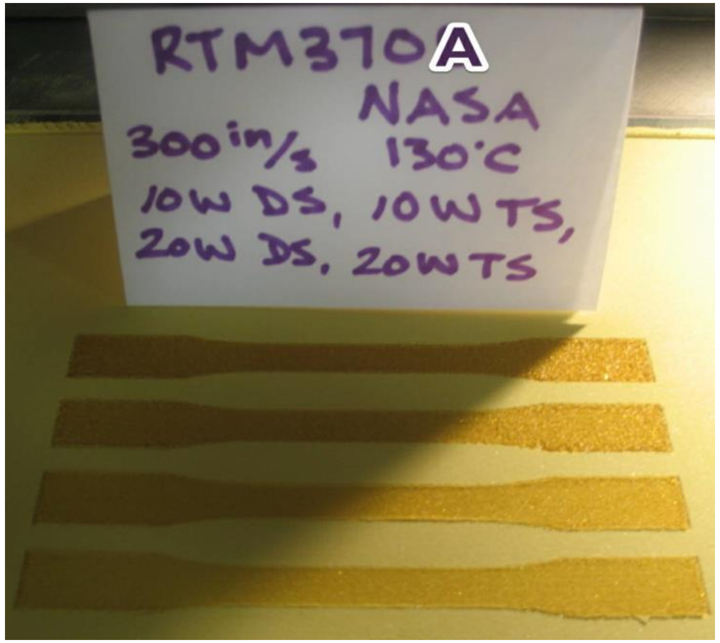
10-20 W agglomeration

30-40 W Balling

Semi-sintered, but no melt

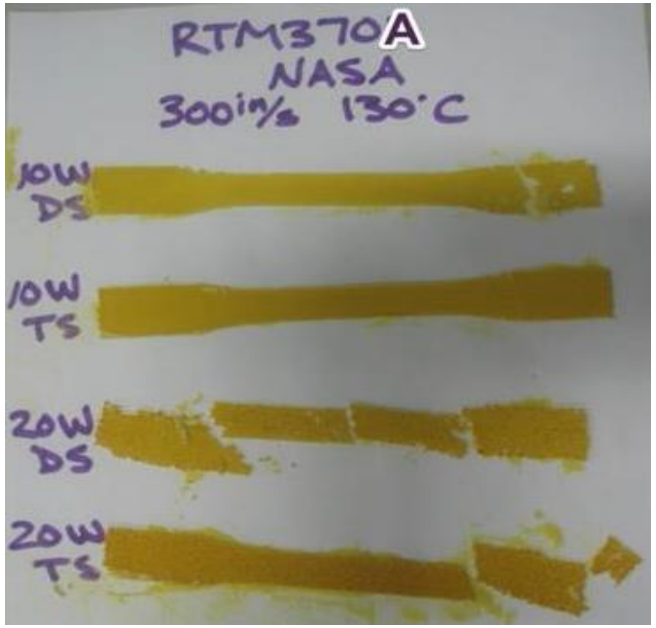
Multiple scans of RTM370 at 130 °C with 10 and 20 watts

(Scan rate = 762 cm/s = 300 in/s, scan spacing = 0.015 cm)



20W TS 20W DS 10W TS 10W DS

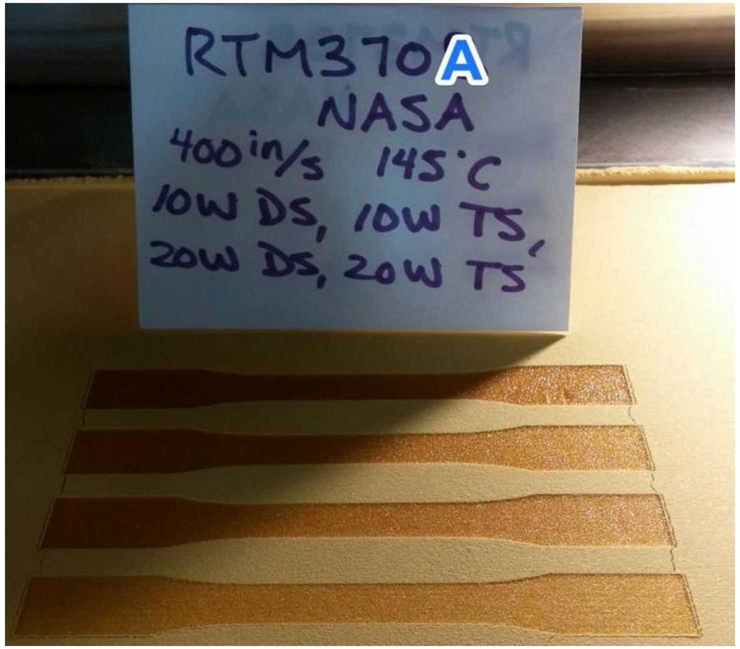
20W/TS has more fusion



Triple scan specimens hold together better & more rigid

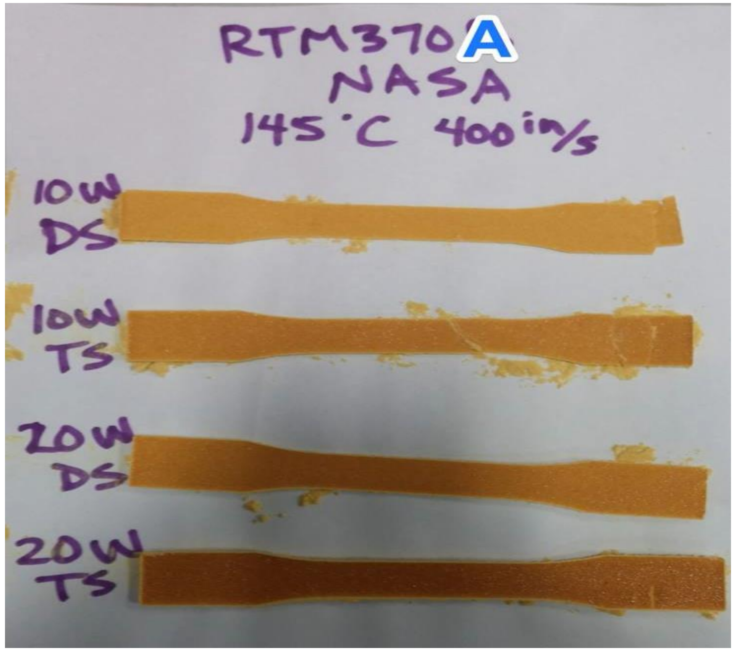
Multiple scans of RTM370 at 145 °C and 10, 20 watts

(Scan rate = 1016 cm/s = 400 in/s, scan spacing = 0.015 cm)



Higher temperature produces more dense parts

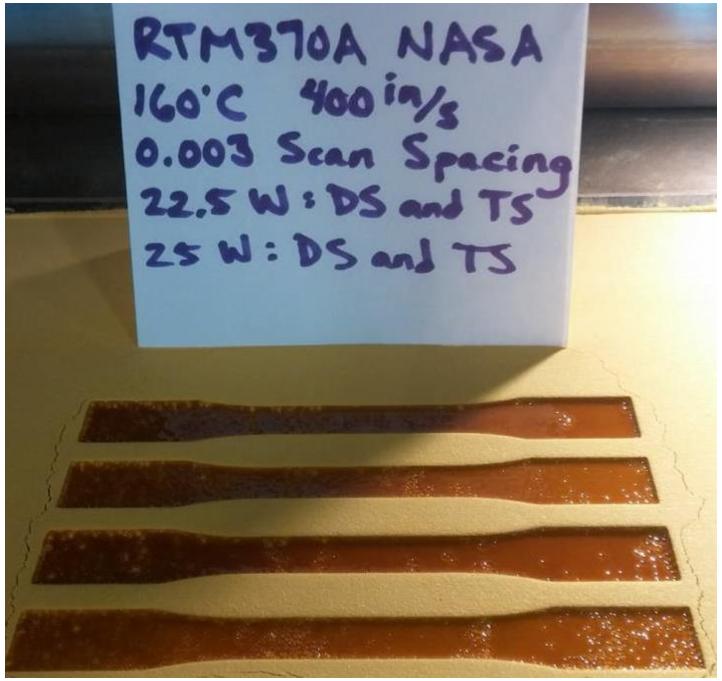
Top: 20W/TS shows sign of melting, but not fully melted



Specimens can be removed, but the powder bed is not agglomerated ⇒ **reusable**

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)

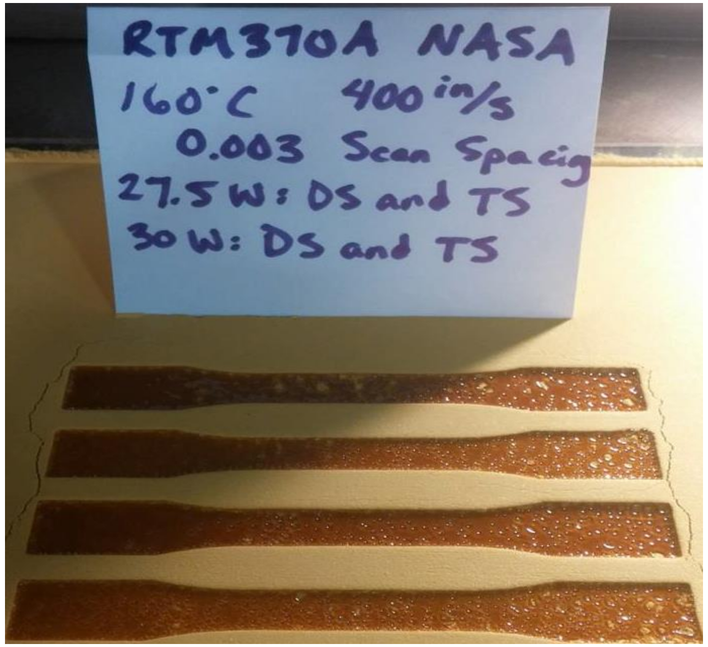


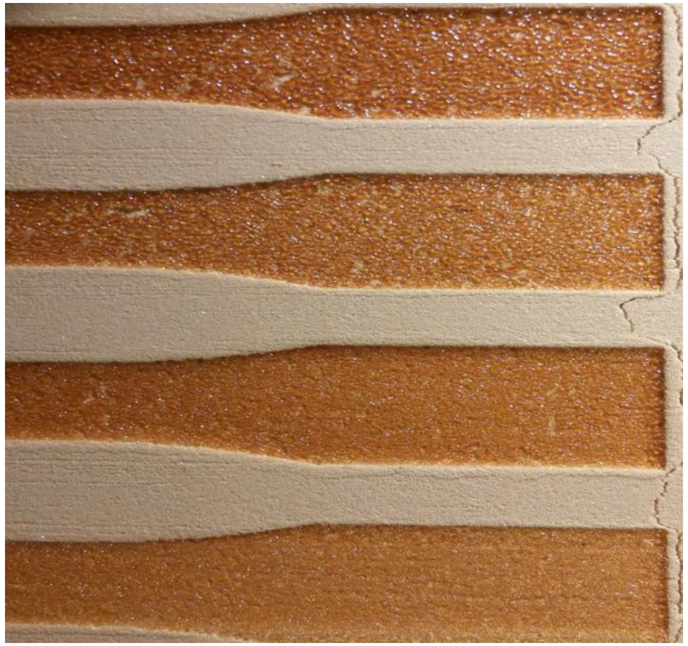
Full melting & flow occurs in all, voids in specimens

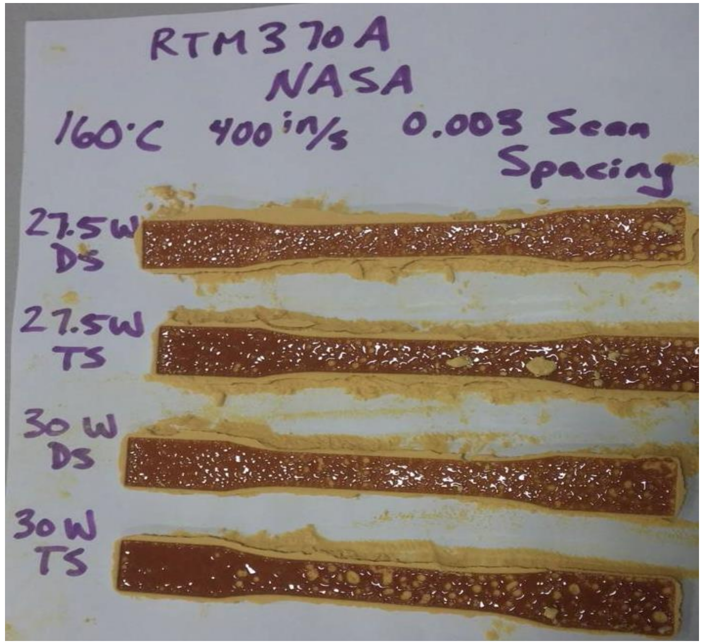
Specimens can be removed

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)







Full melting & flow ⇒ good starting point

Energy densities are above optimal, higher viscosity in resin is desirable

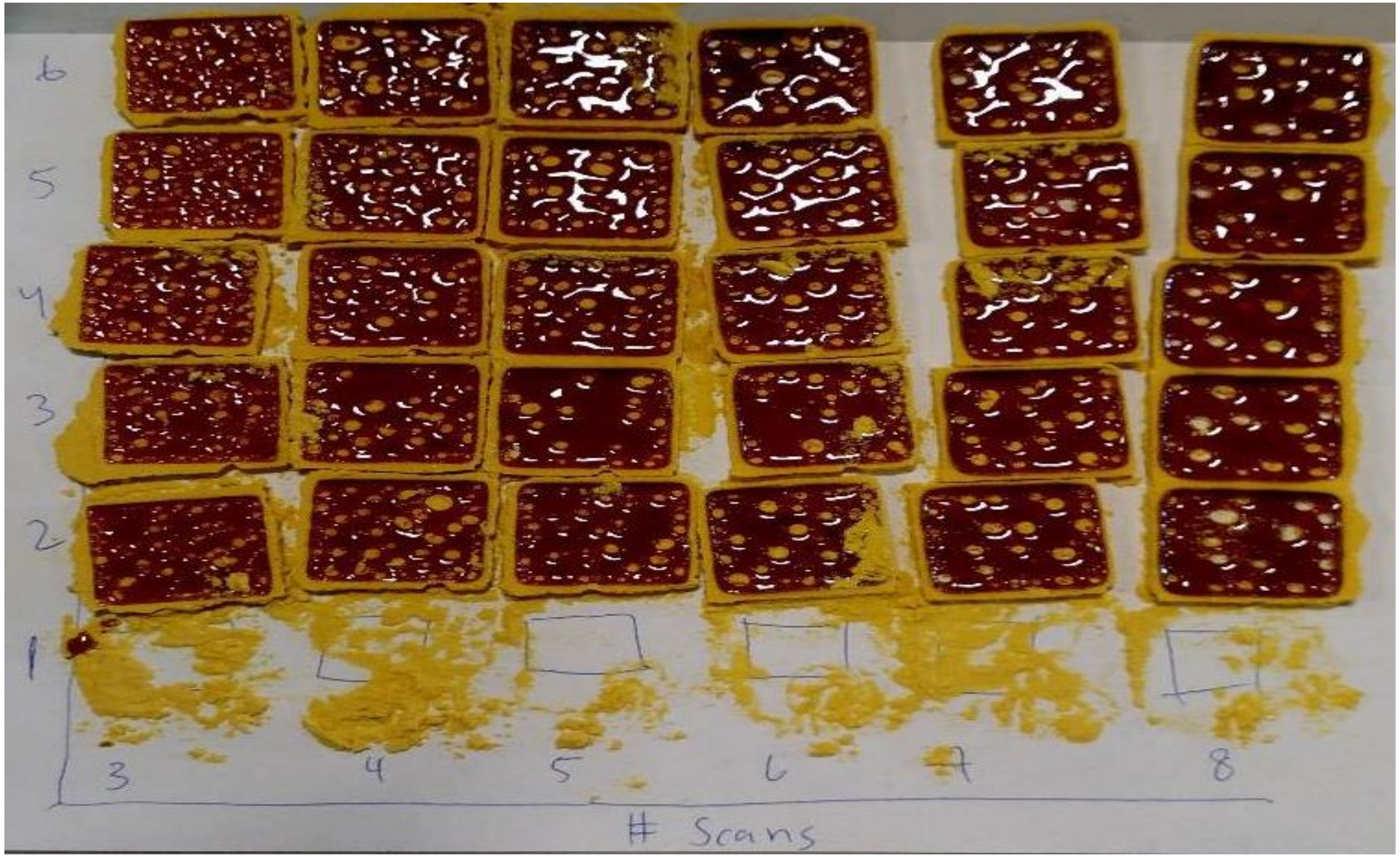
⇒ Spider webbing & voids in specimens

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

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)



Resin chips with multiple scans subjected to postcure in an oven

⇒ **Resin chips were placed on a rod in an oven**

Heat 200 °C

⇒ **Resin chips sagged upon heating to 200 °C**

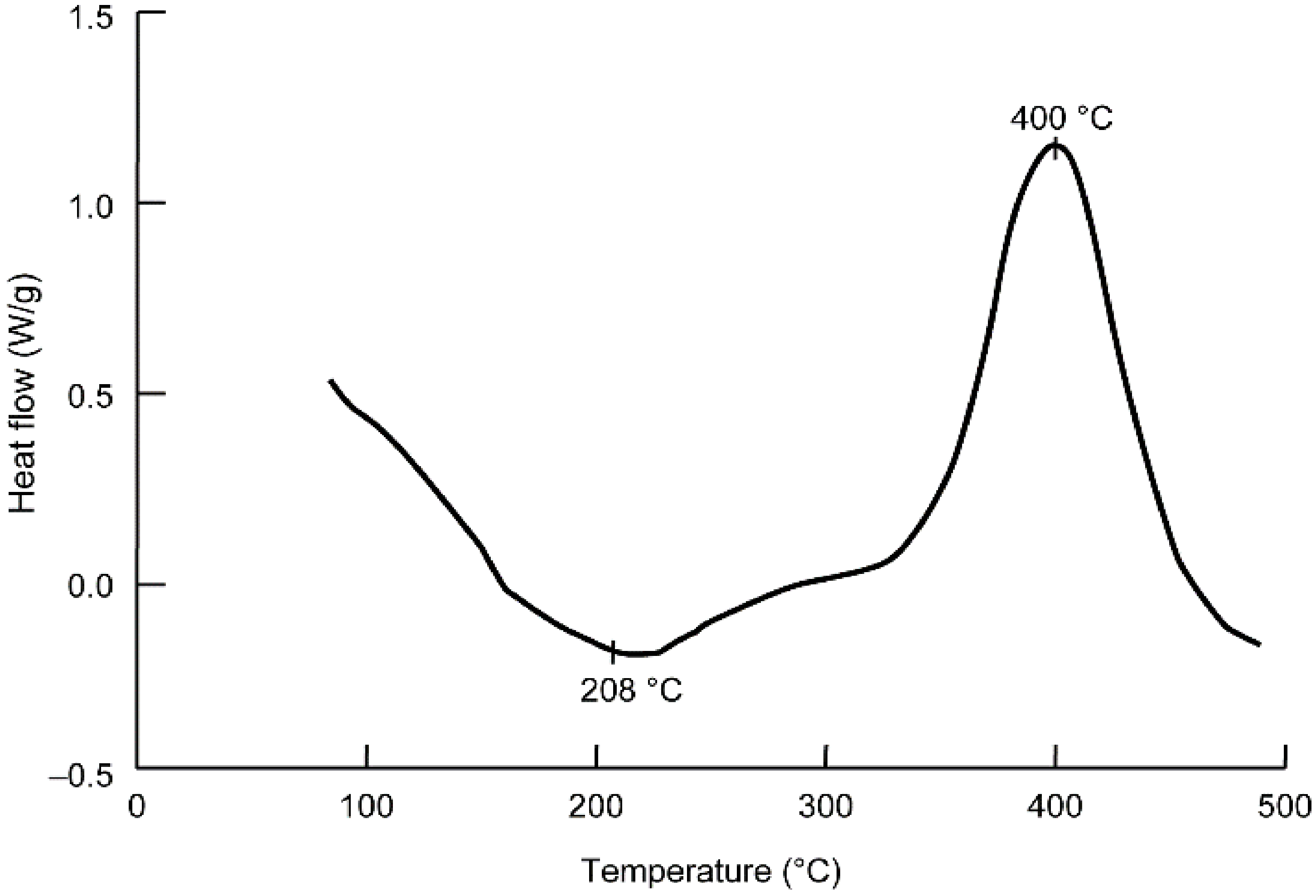
Heat 250 °C

⇒ **Resin chips started melting upon heating to 250 °C**

Heat 300 °C

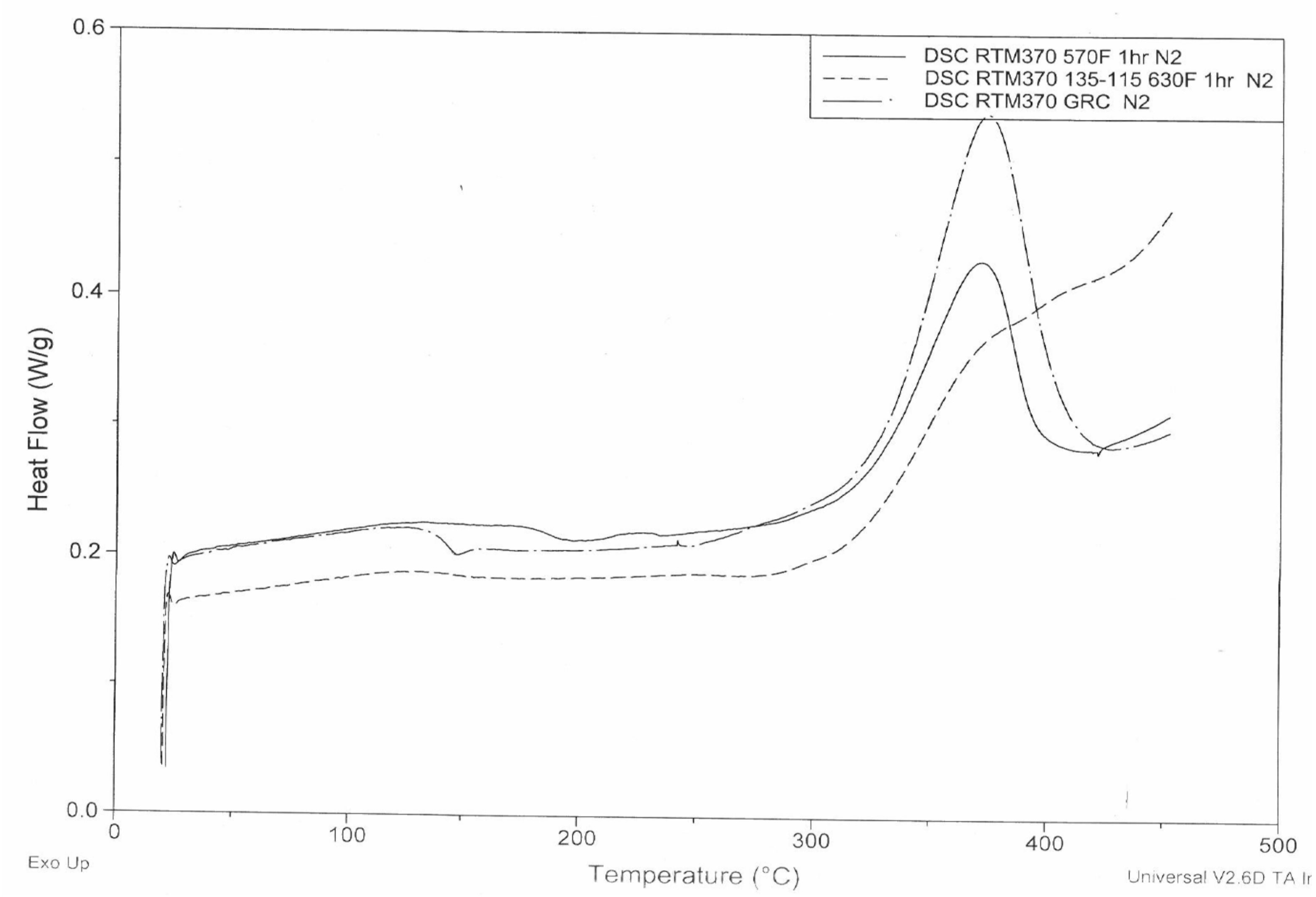
⇒ **Resin chips totally melted at 300 °C**

DSC Thermogram of RTM370 Resin Chips Produced by 8 LS Scans



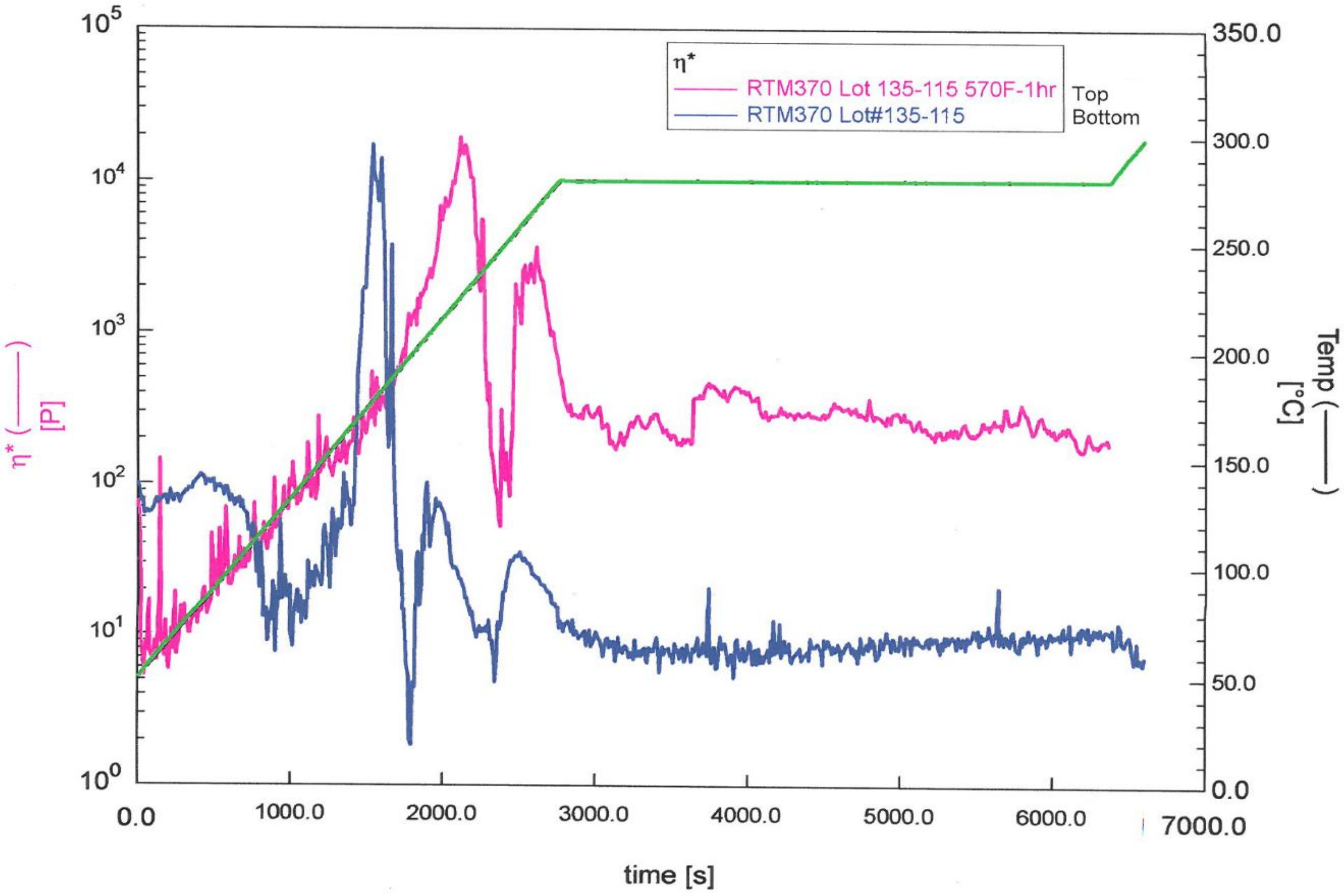
- ♦ Melting at 208 °C
- ♦ Still have huge PEPA exthotherm at 400 °C, indicating lower degree of curing/crosslinking
- ♦ PEPA emdcaps start to cure > 300 °C
- ♦ The specimens are still brittle

DSC Thermograms of RTM370 Resin after Pre-staging at 299 °C (570 °F) and 310 °C (630 °F)



- ♦ Prestaging at 299 °C/1 h induced 50% crosslinking/chain extension
- ♦ Prestaging at 310 °C/1h cured PEPA endcap

Rheology of RTM370 as-received vs pre-staged at 299 °C (570 °F)/1h



- ♦ **RTM370 still melts after pre-staging at 299 °C / 1 h**
  ⇒ complex viscosity (η*) equal to 2×10^2

Conclusion and Future Direction

- ♦ Laser sintering was conducted on a melt-processable thermoset imide oligomer RTM370 which has been fabricated into composites by resin transfer molding (RTM) with 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.
- ♦ Plan to pre-stage RTM370 at 300-310 °C to promote chain extension/crosslinking to increase the molecular weight/viscosity for LS to consolidate 3D-printed specimens.
- ♦ Increasing laser dwelling time to promote crosslinking to enhance integrity of specimens.
- ♦ Develop laser-curable reactive endcaps to enable LS of thermoset resins/composites in AM.

Acknowledgements

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