High-performance liquid crystal thermosets: Resins for marine composite applications

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Extreme Materials for Extreme Applications

High-performance polymers

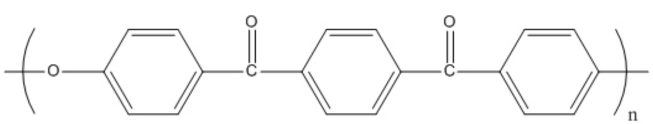
Thermoplastic

- ✓ Shelf life
- ✓ Thermal bonding
- ✓ Post forming possible
- – High Temperature use

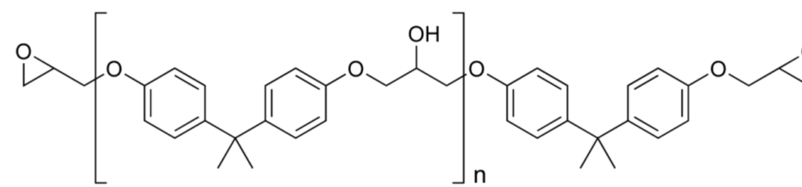
Thermoset

- ✓ Ease of processing
- ✓ High temperature use
- – Shelf life
- – Post forming

Reactive Thermoplastic Polymers

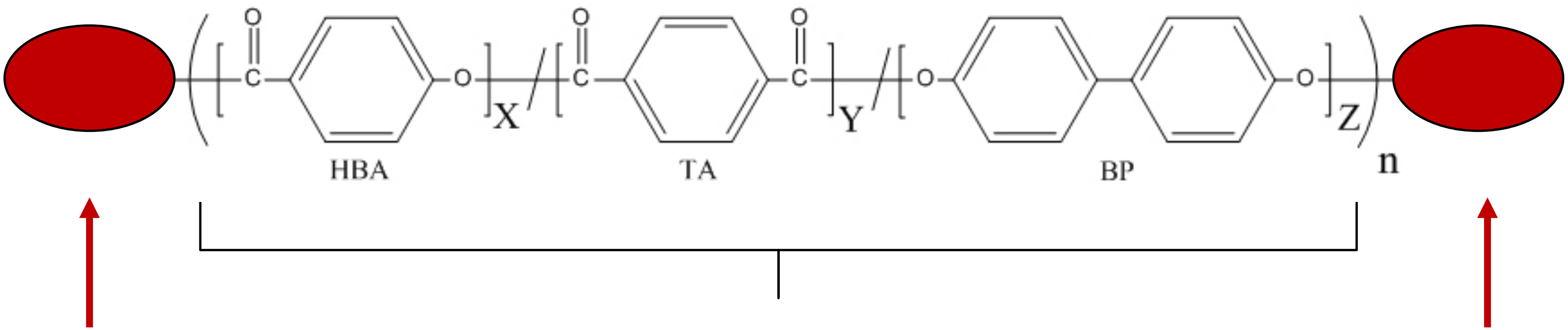


PEKK
T_g 156 °C; T_m 338 °C



bisphenol-A diglycidyl ether epoxy
T_g 190 °C

Reactive Thermoplastic polymers



Thermoplastic oligomer (5-10 K)

- Oligomer state makes low viscous melt processing possible (ideal for composites!)

- Reactive **end-groups** allow for post processing curing: both chain extension and crosslinking is possible

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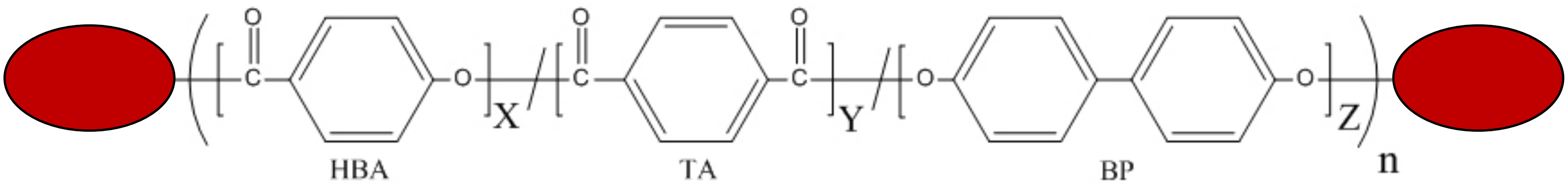
Reactive Thermoplastic polymers



Oligomer is liquid crystalline (LC), which means the polymer chains are rod-like and closely packed

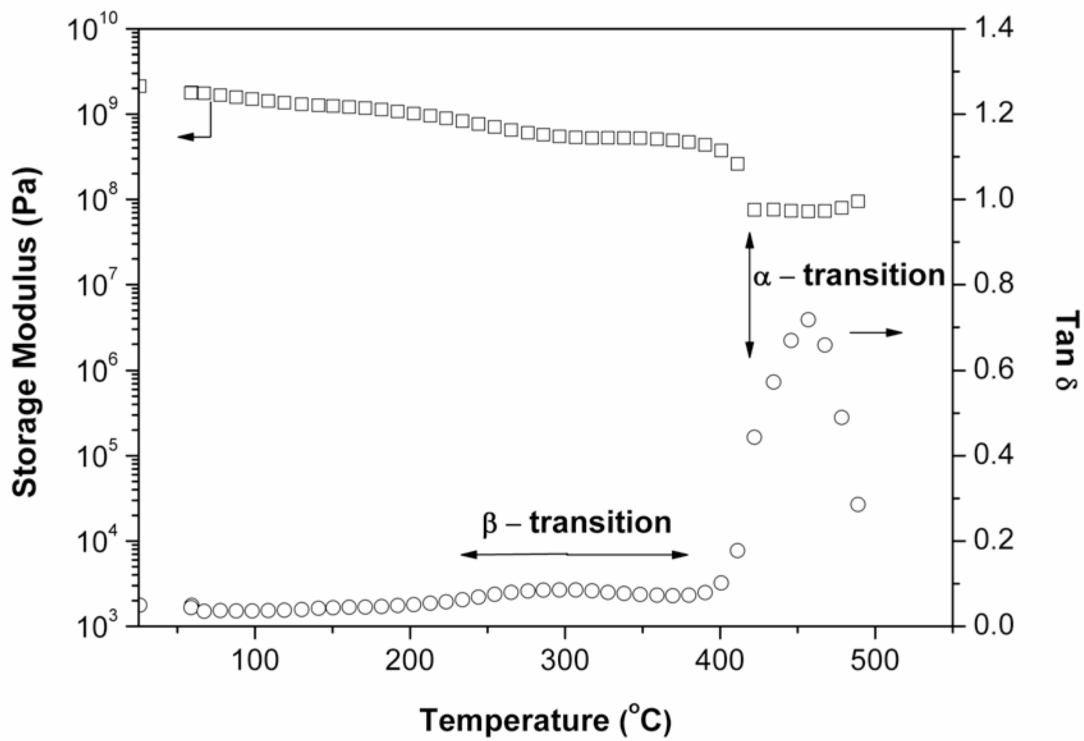
- High after cure Tg (250–350 °C) and $T_d^{5\%}$ (>480 °C)
- Low CTE (below Tg: 5.2 °C^{-1})
- low moisture uptake (< 0.05%) and fluid ingress stable
- Inherently flame ret. (com LCPs are typically UL94-V0)
- LCP have excellent track record in marine applications (stable in UV and salt water and wear resistant)

Thermal properties cured films

When the LC oligomer is cured a Liquid Crystalline Thermoset or **LCT** is obtained

Cured neat films:

- 20 x 5 x 0.25 mm
- Heating rate 2 °C/min
- Frequency 1 Hz



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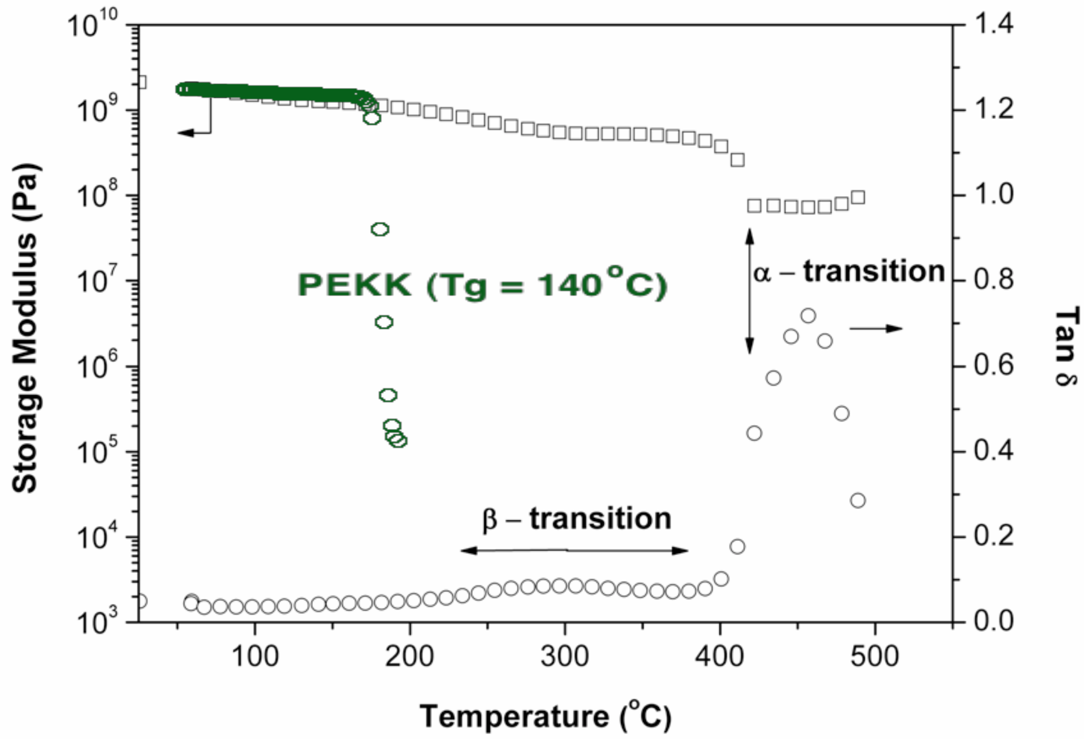

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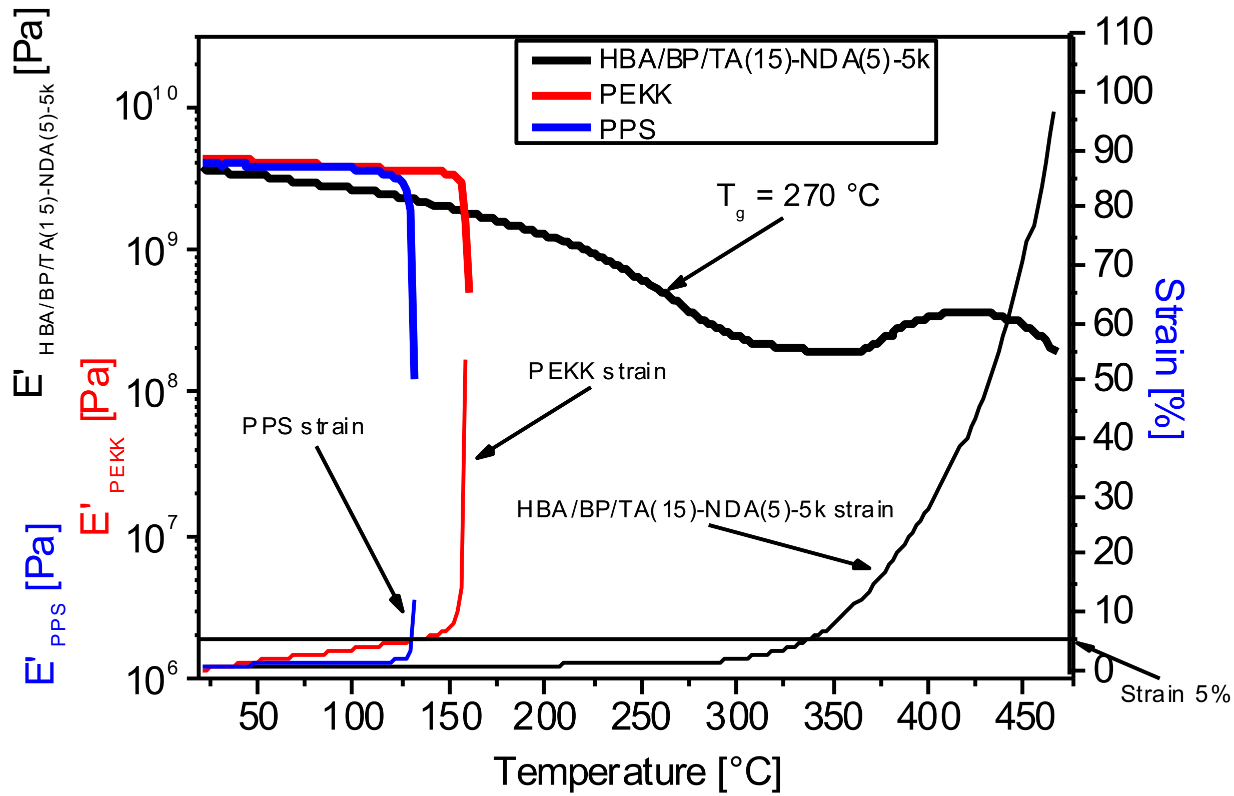
Thermal properties cured films

LCT creep vs PPS and PEKK (neat resins only!)

- 20 x 5 x 0.25 mm
- Heating rate 2 °C/min
- Frequency 1 Hz
- Force: **1–1.2 N**



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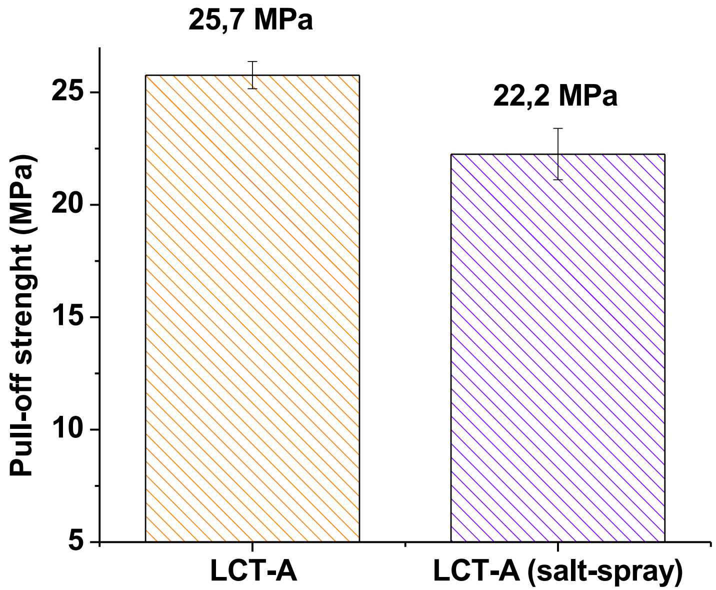
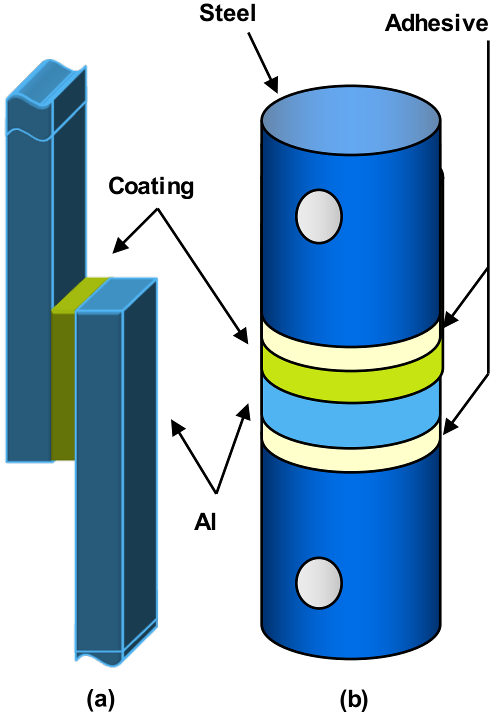
Applications

LCT is typically in film, powder or granulate form (infinite shelf-life) and can be processed into *machinable stock shapes*, foams, *coatings*, ***adhesives*** and ***composites***:



(1000 h salt spray)



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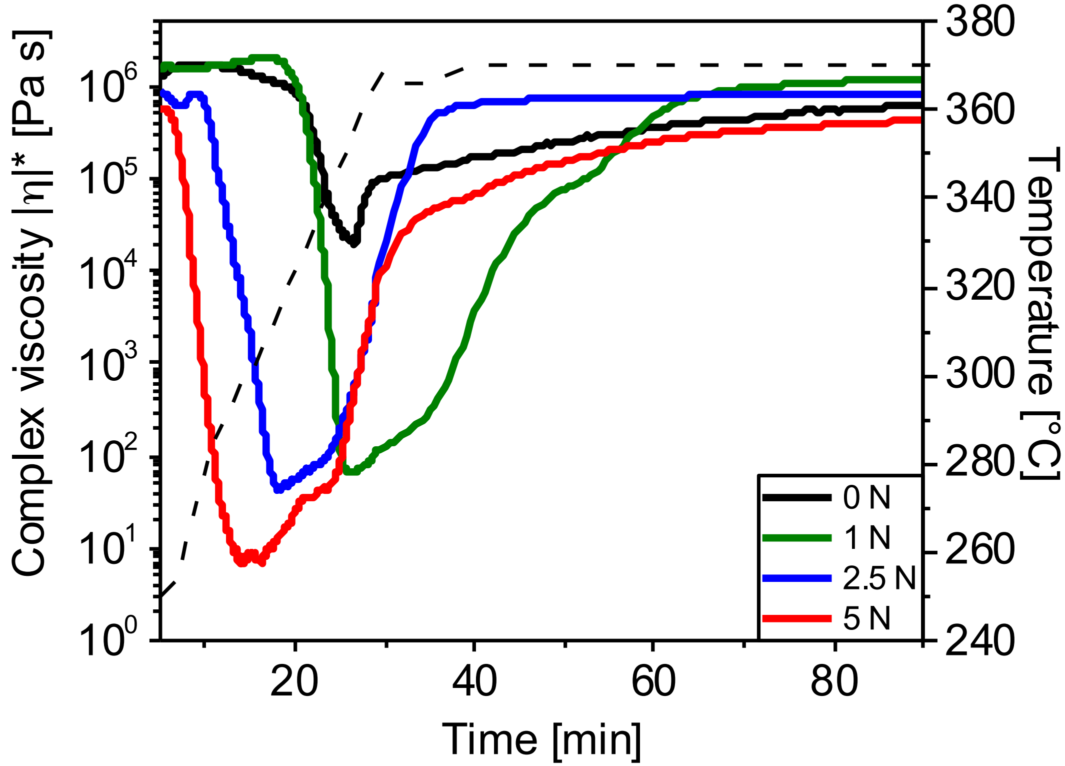
Composite processing

Rheology

Compressed powder pellets, 1% strain, 5 rad/sec, 5 °C/min



LCT suitable for melt prepreging or pultrusion of fibres

Composite processing

- **Composite stack**: 6 plies, 60/40 volume, glass fibre fabric
- **Type of yarn**: EC9 68, 8 harness satin; **Fabric thickness**: 0.23 mm.

LCT powder

5 N – 5k

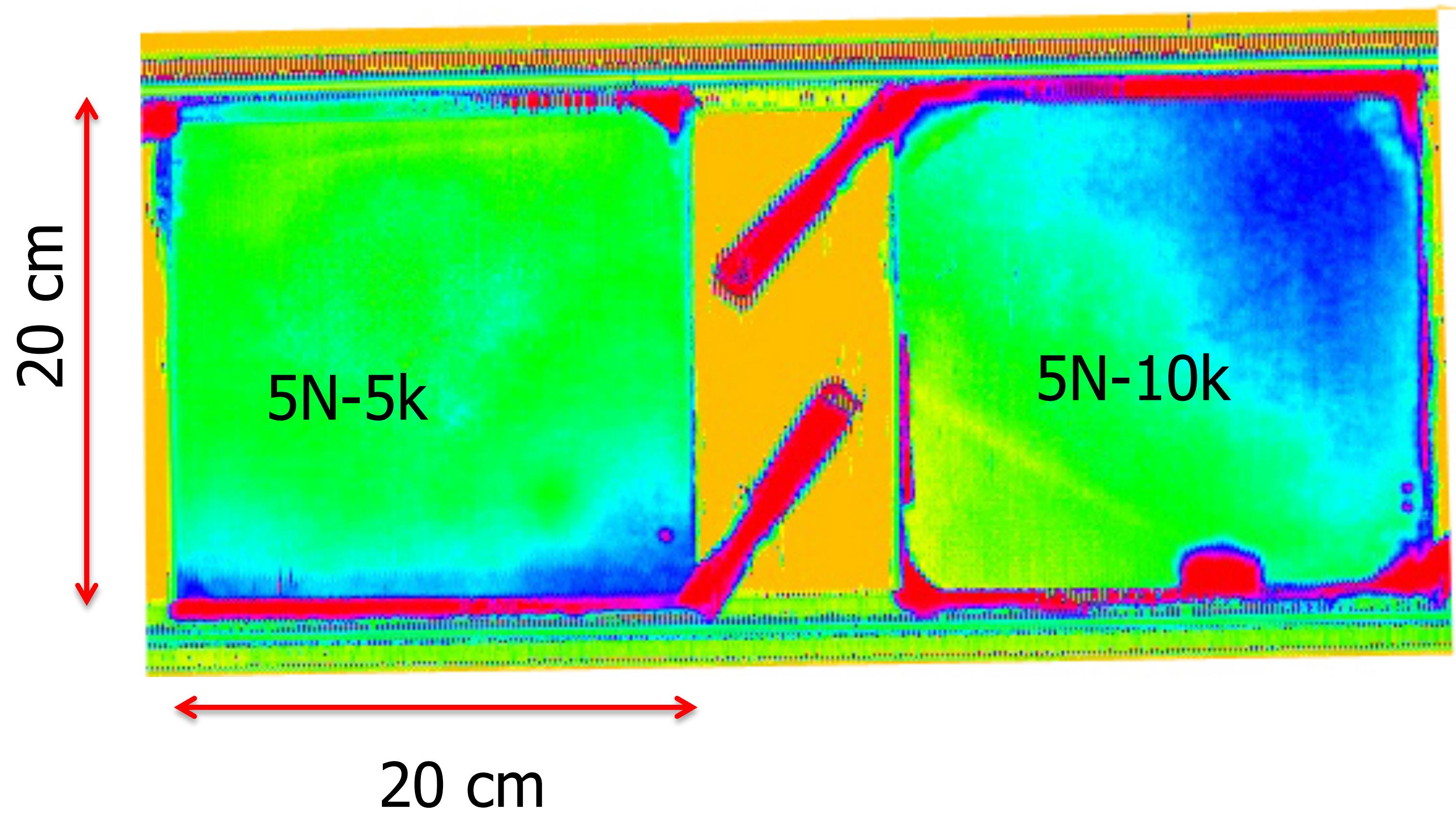
10 cm

5 N – 10k

10 cm

Composite processing

- C-scan inspection of panels



Flame exposure tests

Initial flame exposure test (Peter Coppens, Airborne)

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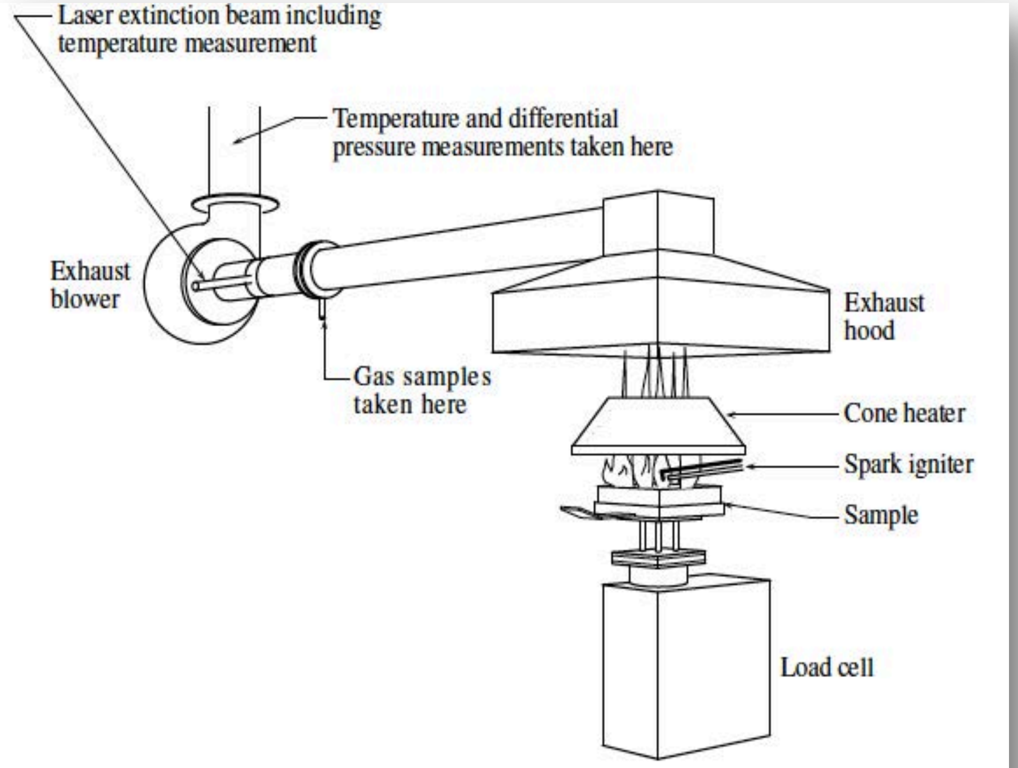
Cone calorimetry tests

Heat release and smoke production according to ISO 5660-1

Test results

Property	Name of variable	Test 1	Test 2	Average value
Flashing (min:s)	t_{flash}	-	-	-
Ignition (min:s)	t_{ign}	01:36	01:50	01:43
All flaming ceased (min:s)*	t_{ext}	02:00	02:06	02:03
Reignition at the edges of the retainer frame (min:s)	t_{reign}	02:39	03:04	02:52
Test time (min:s)	T_{test}	10:00	10:00	10:00
Heat release rate (kW/m^2)	q	See figure 1	See figure 1	
Peak heat release rate (kW/m^2)	q_{max}	78	61	69
Average heat release, 3 min (kW/m^2)**	q_{180}	19	27	23
Average heat release, 5 min (kW/m^2) **	q_{300}	19	26	22
Total heat produced (MJ/m^2) **	THR	14.9	13.2	14.1
Smoke production rate (m^2/m^{2}s)	SPR	See figure 2	See figure 2	
Peak smoke production (m^2/m^{2}s)	SPR_{max}	2.9	2.6	2.8
Total smoke production over the non-flaming phase (m^2/m^2)	TSP_{nonfl}	8.4	17.9	13.2
Total smoke production over the flaming phase (m^2/m^2)	TSP_{fl}	188.8	198.6	193.7
Total smoke production (m^2/m^2) **	TSP	197	216	207
Sample mass before test (g)	M_0	86.3	84.8	85.5
Sample mass at sustained flaming (g)	M_s	86.1	84.6	85.4
Sample mass after test (g) **	M_f	73.3	72.6	73.0
Average mass loss rate (g/m^{2}s) **	$MLR_{ign-end}$	2.7	2.6	2.7
Average mass loss rate (g/m^{2}s) **	MLR_{10-90}	2.9	2.9	2.9

Per Blomqvist (SP)



Schematic drawing of the Cone calorimeter, ISO 5660.

Cone calorimetry tests

Heat release and smoke production according to ISO 5660-1

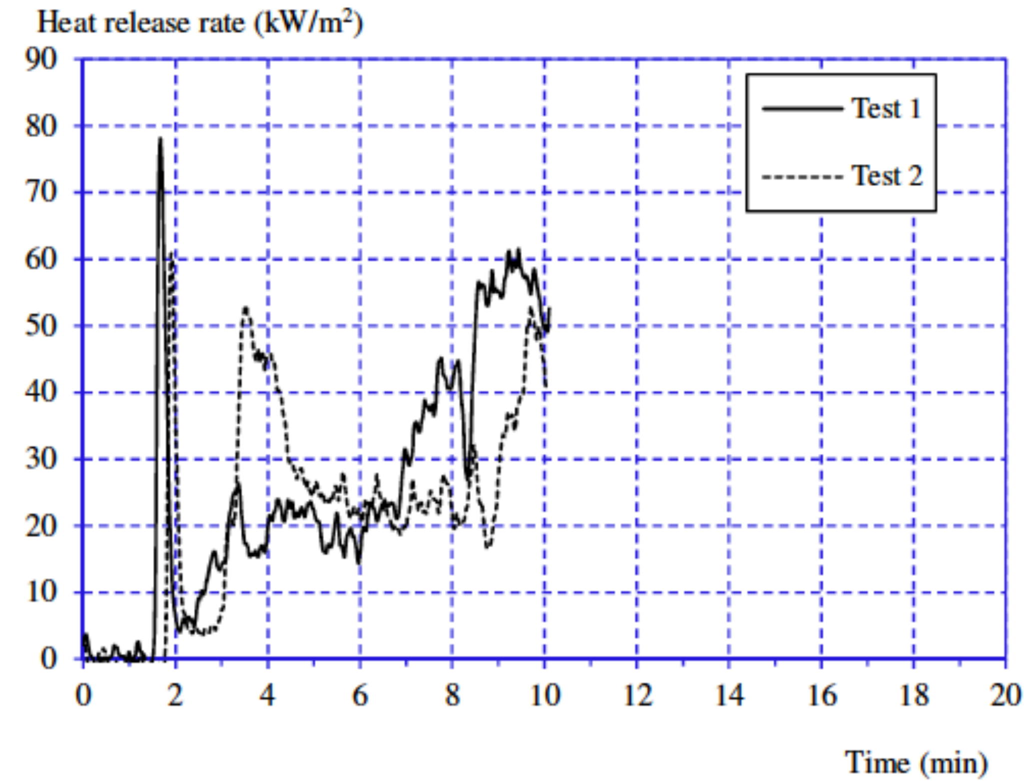


Figure 1 Heat release rate for LCT Glass reinforced laminate, duplicate tests at an irradiance of 50 kW/m².

Cone calorimetry tests

How to compare to a well-known epoxy resin?

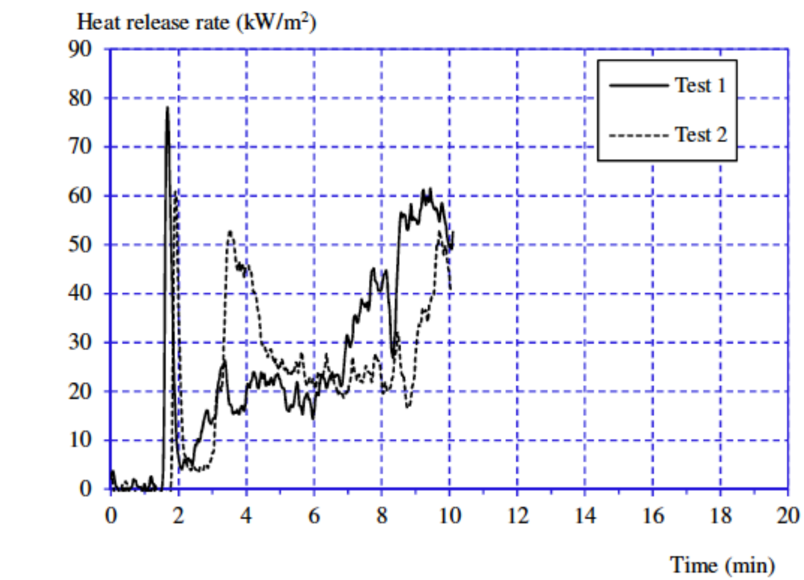
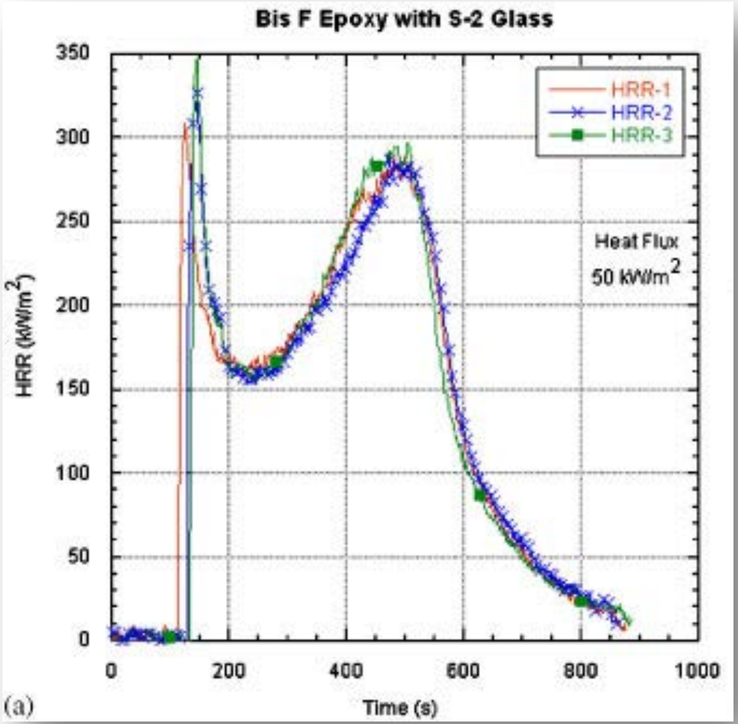


Figure 1 Heat release rate for LCT Glass reinforced laminate, duplicate tests at an irradiance of 50 kW/m².



Bis F epoxy/glass (30/70). ASTM E-1354-04 at 50kW/m^2

Fire Mater 2009; 33:323–344.

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Cone calorimetry tests

Smoke production rate

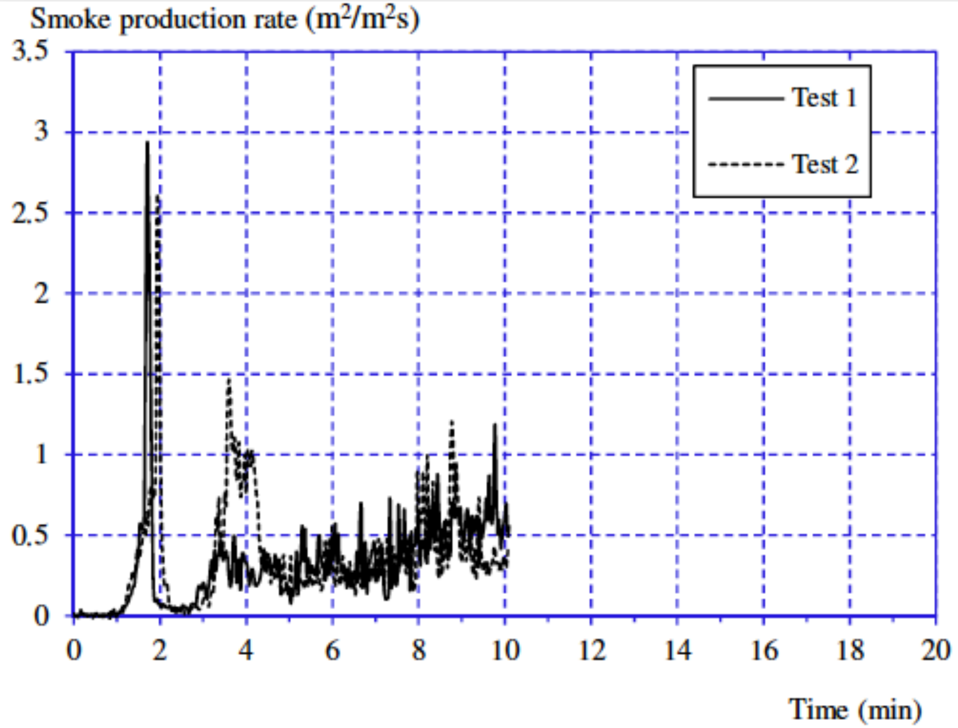

Figure 2 Smoke production rate for LCT Glass reinforced laminate, duplicate tests at an irradiance of 50 kW/m^2.

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Cone calorimetry tests

Test results from ISO 5660-1 were used to predict the behaviour of glass/LCT in a ISO 9705 room-corner test

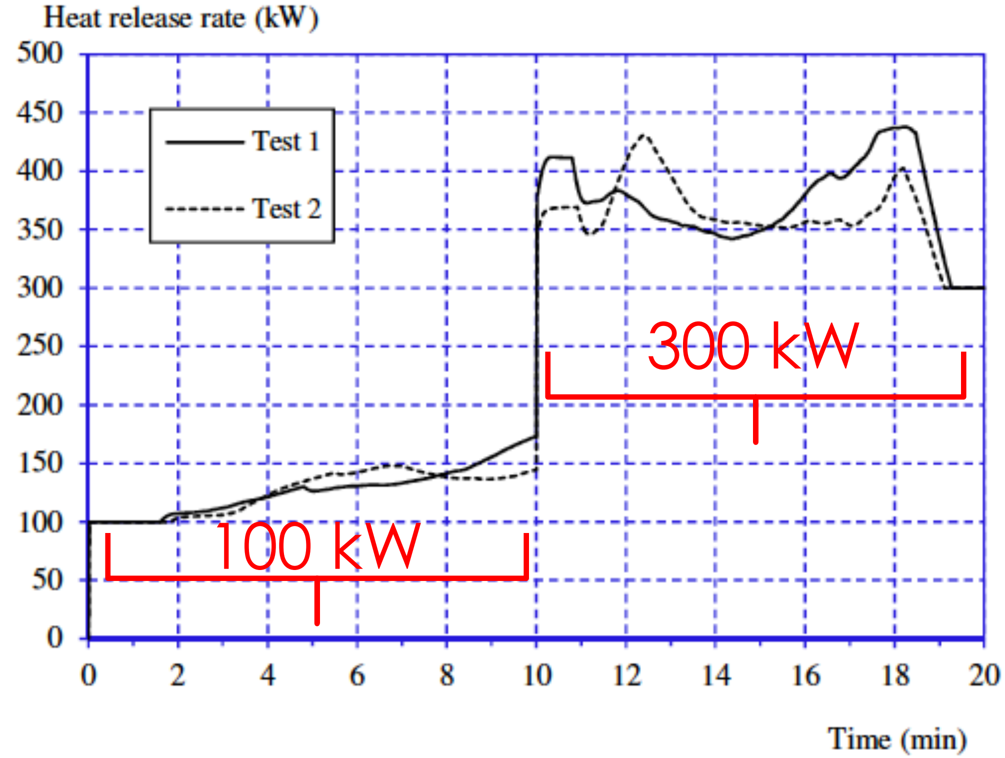

Figure 4:1 Simulated HRR in the ISO 9705 test with input data from duplicate Cone calorimeter tests at 50 kW/m² with "LCT Glass reinforced laminate".

Conclusions

- Cured LC thermosets (LCTs) offer high Tg's (200–350 °C), low creep, low CTE's, low moisture absorption and fluid stability
- Reactive LC oligomers exhibit low melt viscosities, which makes them ideal candidates for (highly filled) short- and continuous fibre reinforced composites
- LCT can be processed into composite panels that can be thermally formed on-site (e.g. stamp forming)
- LCT–glass composites show good room temperature mechanical properties
- LCT-glass composites exhibit low flammability and hence show promise for marine structural (composite), coating, insulating foam and adhesive applications

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SP Group
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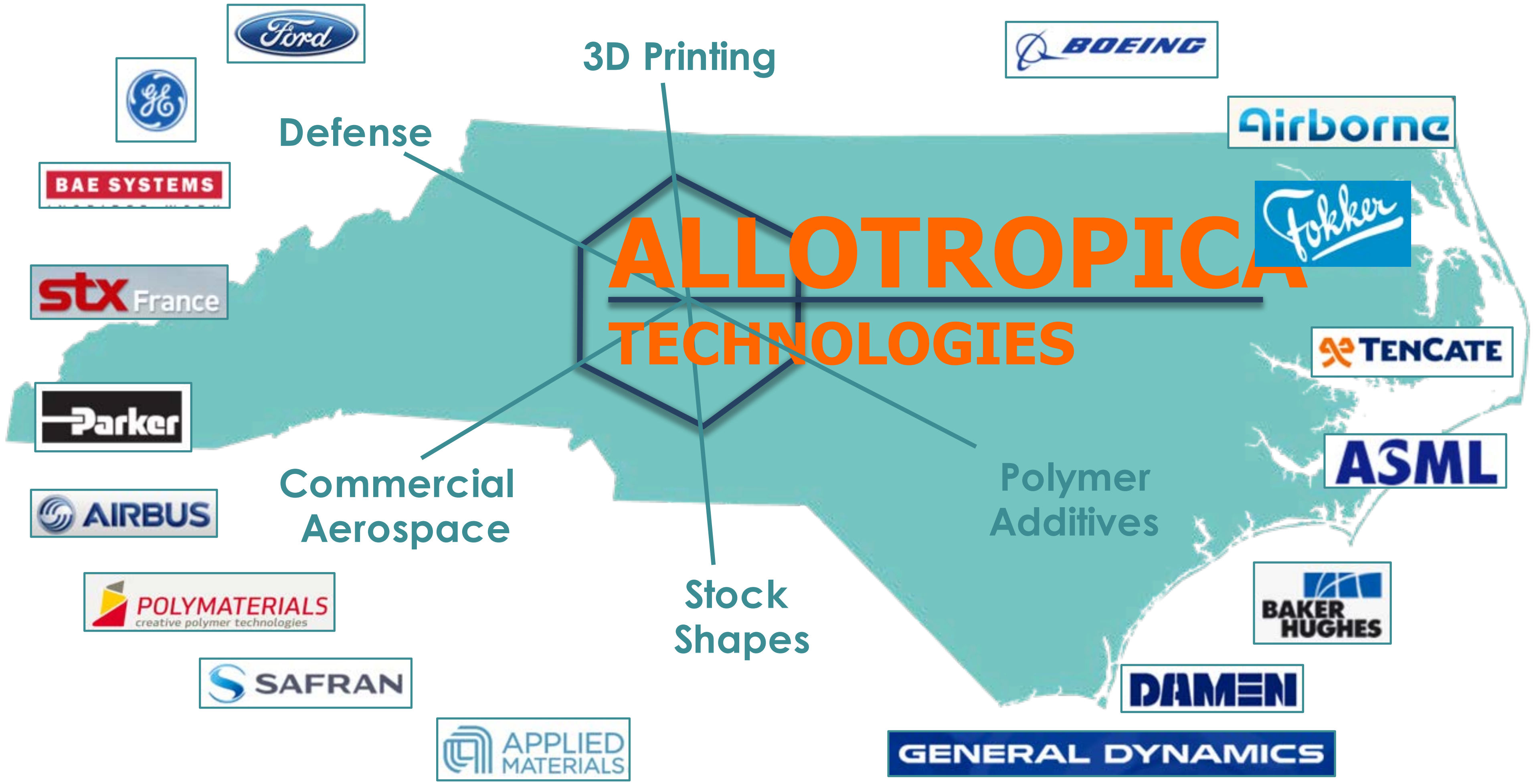
and Promoulding



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