Reactive Processing: Cure Time vs. Heat Transfer

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Reactive Processing: Cure Time vs. Heat Transfer

- Why thermoplastics may be advantageous.
- How can you do RTM or VARTM with thermoplastics?
- Commercially available thermoplastics infusion systems.
- Heat transfer and chemical kinetics.
- Phase Change Materials (PCMs)
Why Thermoplastics?

Plastics are characterized according to their **response to temperature:**

**Thermoplastics - soften and flow upon heating:**

- $T_g$ - Glass Transition Temperature (beginning of chain motion over several segments)
- $T_m$ - Melting Temperature (chains can self-diffuse) (for semi-crystalline polymers)

Some thermoplastics are amorphous glasses without melting temperatures.

**Thermosets - rigid until thermal decomposition**

**Epoxies, unsaturated polyesters, and other network forming materials that are used today**
Why Thermoplastics?

End-of-life composite part or production waste

Grinding

20 – 40%

Compounding (ABS, PLA, PMMA, etc.)

Short fiber compound

Injection molding of short fiber compound

NEW Composite part

PROPERTIES

<table>
<thead>
<tr>
<th></th>
<th>Commercial compound ABS-GF20</th>
<th>ABS + 40% recycled Elium®</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection</td>
<td>Same conditions</td>
<td></td>
</tr>
<tr>
<td>Stiffness</td>
<td>4.9 GPa</td>
<td>6.9 GPa</td>
</tr>
<tr>
<td>Strength</td>
<td>69 MPa</td>
<td>76 MPa</td>
</tr>
<tr>
<td>Impact Charpy</td>
<td>13 kJ/m²</td>
<td>22 kJ/m²</td>
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Improvement of short fiber ABS compound when recycling Elium® composites.
Why Thermoplastics?

- When “cured” ELIUM® resin remains **fully** thermoplastic!
  - Allows for post-forming
  - Excellent aesthetics; clarity and surface finish

**Forming conditions**
- ~200°C and 15 - 20 bar applied pressure (~250 PSI)
- Degree of draw and applied pressure are dependent on thickness and reinforcement type used in the part
Thermoplastic infusion

VARTM – Vacuum Assisted Resin Transfer Molding.

Low viscosity resins infused and then cured in mold / autoclave.

Not injecting high viscosity preformed polymers!
Arkema Innovation

“Acrylate based”
- Dana Swan
**Johns Manville Innovation**

**United States Patent**

Shooshtari et al.

Patent No.: US 8,378,094 B2  
Date of Patent: Feb. 19, 2013

**Polymerization Initiators for Fiber-Reinforced Polymer Composites and Materials Made from the Composites**

Inventors: Kiarash Alavi Shooshtari, Lit (US); Jawed Asrar, Englewood (US); Rajappa Tadepalli, Litl (US); Thomas Burghardt, Par (US); Klaus Friedrich Gleich, Highlands Ranch, CO (US)

Assignee: Johns Manville, Denver, CO (US)

**United States Patent**

Burghardt et al.

Patent No.: US 8,293,322 B2  
Date of Patent: Oct. 23, 2012

Surfaces Containing Coupling Activator Compounds and Reinforced Resins Produced Therefrom

Inventors: Thomas Burghardt, Parker, CO (US); Jawed Asrar, Greenwood Village, CO (US); Klaus Friedrich Gleich, Highlands Ranch, CO (US)

Assignee: Johns Manville, Denver, CO (US)

**United States Patent Application Publication**

Gleich et al.

Pub. No.: US 2010/0305269 A1  
Pub. Date: Dec. 2, 2010

Methods and Systems for Making Reinforced Thermoplastic Composites, and the Products

Inventors: Klaus Friedrich Gleich, Highlands Ranch, CO (US); Jawed Asrar, Englewood, CO (US); Thomas E. Burghardt, Parker, CO (US); Rajappa Tadepalli, Highlands Ranch, CO (US)

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  B29C 33/02  
  B01J 19/00  

- U.S. Cl.  
  524/606; 264/240; 422/138

**Abstract**

Various methods and systems of making inorganic fiber/flake reinforced composites having a thermoplastic matrix are disclosed. The methods and systems include forming a reinforced composite from a mixture of a thermoplastic matrix, a reinforcing filler, and a coupling agent, and then shaping the mixture into a desired formation.
Experiments at CSM

- Samples of methylmethacrylate (MMA) monomer immersed in constant T bath.
- J-Type thermocouples with a data logger.

Wall temperature
25 °C
2 hour cure time

![Graph showing Temperature vs Time](chart.png)

- Boiling Temperature
- Induction time

![Image of samples](samples.png)
Experiments at CSM

Elium™ has a lower exotherm.

Initiator is analogous to hardener / curative in epoxy systems.

Less initiator means slower reaction and lower peak temperatures due to increased time for heat transfer.
Chemical kinetics coupled to heat transfer and including “gel effect” due to diffusional limitations
Cross-Cutting: Model Development

Qualitative description based on literature values

Determining parameter set for quantitative description
RAVEN is a desktop composites processing analysis program that allows users to **design**, **optimize**, and **troubleshoot** processing of composites.

**RAVEN is used for:**
- Cure cycle optimization
- Thermal profiling
- Troubleshooting
Rheology and shrinkage data for simulation

Elium reaction rheology experiments take place in two steps:

1) Measure the viscosity as a function of time at a constant shear rate of 100 1/s with the gap fixed at 1 mm:

\[ \eta = 1 + \frac{1}{3} \left( \frac{h - h_0}{h_0} \right)^3 - 1 \]

\( h = \) gap height
\( h_0 = \) initial gap height

2) When the torque on the geometry reaches a cutoff value, switch to an oscillatory measurement at 3.33 rad/s and allow the gap to change to produce an applied normal force of 0.5 N:
• Complementary facilities at Johns Manville in Littleton, Colorado (*just 15 miles away*).
Additional CSM capabilities

- Zeiss X-ray CT (computed tomography)

- CT scan to see the skeleton of the composite!
  - 0 / 90 / 0 glass fiber
Heat imaging during infusion

- Elium with 3 wt% initiator package
- 40 minutes time lapse
- Frame speed is 1 min or 30 s during rapid temperature change.
Phase Change Materials (PCMs)

- Recall:
  - "Sensible" heat is energy to raise the T of a given phase (water in this graph).
  - "Latent" heat is the energy needed to change phases; to melt a crystal for example. This is more properly the "heat of fusion".
  - *Latent heats are much larger than sensible heats.*
Phase Change Materials (PCMs)

• PCMs have become widely used:
  • Domino Pizza “Heat Wave” bag
  • Every laptop has a “heat pipe” which uses liquid to gas vaporization
  • Outlast Technology (now part of CoorsTek) adopted NASA space suit technology to outdoor clothing.
Effect of commercial PCMs on Elium™

PCMs enable shorter cycle times!

Same initiator composition

20
30
40
50
60
70
80
90
100
0 10 20 30 40

Temperature (°C)

Time (s)

Elium
Elium +10 wt% PCM
Elium +20 wt% PCM

Crystallization of PCM

Time (min)

5.0 wt%
5.0 wt% (with PCM)
3.0 wt%
Heat imaging during infusion

Without PCM

With PCM

\[ T_{\text{peak}} = 104 \, ^{\circ}\text{C} \]

\[ T_{\text{peak}} = 84 \, ^{\circ}\text{C} \]

Tpeak = 104 °C  \hspace{2cm}  Tpeak = 84 °C

Slow motion during the curing reaction

NDE – cold spots reveal problems and in situ emission FTIR can provide cure information
Conclusions

• Thermoplastic composites hold several advantages
  – Recyclable
  – Reformable
  – Potentially lower cost

• Cycle times for RTM and VARTM are presently too long for very high volume automotive applications.

• Phase change materials are well-known and commercially available and used in many applications but have not been exploited in composites manufacturing.

• Juditious use of PCMs can decrease cycle times with only modest decreases in physical properties
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