CELLULOSE NANOCRYSTALS FOR LIGHTWEIGHT SHEET MOLDING COMPOUNDS COMPOSITES

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G.W. Woodruff School of Mechanical Engineering and School of Materials Science and Engineering
Georgia Institute of Technology
OUTLINE

- Motivation
- Goal and Objectives
- Background
- Feasibility study of using basalt fibers
- Light-weighting of sheet molding compounds
- Conclusions
LIGHT-WEIGHTING IN THE AUTOMOTIVE INDUSTRY

- Governamental regulations
- Societal/customer pressure
  - Better fuel economy
  - Less greenhouse gas emissions
  - Better performance

GOALS AND OBJECTIVES

CREATE LIGHTWEIGHT SHEET MOLDING COMPOUND (SMC) COMPOSITES FOR AUTOMOTIVE APPLICATIONS

1. Study feasibility of using basalt fibers as alternative for glass fibers
2. Reduce weight of SMC parts by introduction of cellulose nano-crystals
SHEET MOLDING COMPOUND - APPLICATIONS
Unique SMC line:

- Similar to industrial SMC machines
- Smaller width
  (0.3 m vs. 0.9 - 1.5 m)
SMC PROCESSING

(1) Image of a machine processing material.

(2) Image of a roll of material and a sheet of material.

(3) Image of a person applying material to a surface.

(4) Image of stacked material sheets.
Fiber content < 40 %
- 1.5h pre-conditioning → increase viscosity for handling
- Pressure: 125 kPA

Fiber content > 40 %
- no pre-conditioning → keep viscosity low for good fiber impregnation
- Pressure: up to 430 kPa
WHAT IS BASALT?
WHY USING BASALT FIBERS?

- Extrusive volcanic rock
- Rapid cooling of basaltic lava
- Mixture of different silicates
- Most common rock type

- Superior hygrothermal and chemical stability
- Less energy-extensive manufacturing compared to GF
- No additives required
- High availability of basalt

→ Potential lower economical cost
→ Ecofriendly
## BASALT FIBER VS. GLASS FIBER

<table>
<thead>
<tr>
<th></th>
<th>Basalt fiber</th>
<th>Glass fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm(^3))</td>
<td>2.75*</td>
<td>2.54*</td>
</tr>
<tr>
<td>Filament diameter (μm)</td>
<td>10±1</td>
<td>10±1</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>87±5*</td>
<td>75±5*</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>4500±400</td>
<td>4100±300</td>
</tr>
<tr>
<td>Price ($/lb)</td>
<td>1.4*</td>
<td>1-2*</td>
</tr>
</tbody>
</table>

* Data provided by suppliers
- Same curing behavior for BF/epoxy and GF/epoxy
- Same curing cycles can be applied for both
### INTERFACIAL SHEAR STRENGTH (IFSS)

**Measured distance**

<table>
<thead>
<tr>
<th></th>
<th>BF/epoxy</th>
<th>GF/epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average Fragment Length (μm)</strong></td>
<td>729.7±62.4</td>
<td>758.0±98.9</td>
</tr>
<tr>
<td><strong>Interfacial Shear Strength (MPa)</strong></td>
<td>42.7±6.1</td>
<td>39.8±8.1</td>
</tr>
</tbody>
</table>
SMC PLATES

• 25 wt% fiber content for both composite types
• Cut into test coupons for mechanical testing
MECHANICAL PROPERTIES

- Tensile properties (ASTM D638)
- Flexural properties (ASTM D790-02)

<table>
<thead>
<tr>
<th>Strength (MPa)</th>
<th>25GF/epoxy</th>
<th>25BF/epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus (GPa)</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

Graph showing mechanical properties for 25GF/epoxy and 25BF/epoxy.
**DENSITY AND VOID CONTENT**

- **Theoretical density:**
  \[ \rho_{\text{theoretical}} = \frac{1}{(w_f/\rho_f)+(w_m/\rho_m)} \]

- **Experimental density (ASTM D-792):** water displacement method

- **Void content (ASTM D2734-16):**
  \[ V_{\text{void}} = 100 \times \frac{\rho_{\text{theoretical}} - \rho_{\text{exp}}}{\rho_{\text{theoretical}}} \]

<table>
<thead>
<tr>
<th></th>
<th>25BF/epoxy</th>
<th>25GF/epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fiber density (g/cm³)</td>
<td>2.75*</td>
<td>2.54*</td>
</tr>
<tr>
<td>Theoretical composite density (g/cm³)</td>
<td>1.35</td>
<td>1.31</td>
</tr>
<tr>
<td>Experimental composite density (g/cm³)</td>
<td>1.29±0.04</td>
<td>1.25±0.01</td>
</tr>
<tr>
<td>Void content (vol-%)</td>
<td>5±1</td>
<td>5±1</td>
</tr>
</tbody>
</table>

* Data provided by suppliers
SPECIFIC MECHANICAL PROPERTIES (DIVIDED BY DENSITY)

- Tensile properties
- Flexural properties

**Specific Modulus (GPa/g/cm³)**
- **25GF/epoxy**
- **25BF/epoxy**

**Specific Strength (MPa/g/cm³)**
- **25GF/epoxy**
- **25BF/epoxy**
FRACTURE SURFACE MORPHOLOGY

25BF/epoxy

25GF/epoxy
IMPACT STRENGTH

Impact Energy (kJ/m²)

25GF/epoxy  25BF/epoxy
CONCLUSIONS

BF-reinforced SMC composites do not show advantages in terms of lightweighting.

However, they are a potential cost-efficient and ecofriendly alternative to GF/epoxy composites.
WHAT IS CELLULOSE?

# CELLULOSE NANO-CRYSTALS

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (nm)</td>
<td>138±22 *</td>
</tr>
<tr>
<td>Width (nm)</td>
<td>6.4±0.6 *</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.6 **</td>
</tr>
<tr>
<td>Tensile strength (GPa)</td>
<td>7.5 – 7.7 **</td>
</tr>
<tr>
<td>Elastic modulus in axial direction (GPa)</td>
<td>110 – 220 **</td>
</tr>
<tr>
<td>Elastic modulus in transverse direction (GPa)</td>
<td>10 – 50 **</td>
</tr>
</tbody>
</table>

* Girouard et al., Polymer 2015; 68: 111-121.
LIGHT-WEIGHTING OF SMC COMPOSITES BY ADDING CELLULOSE NANO-CRYSTALS (CNC)

Introducing CNC to the **matrix**

Coating the fibers with **CNC**

Increasing the **mechanical properties** of the matrix

Increasing the **Interfacial Shear Strength** between fiber surface and matrix

Ability to **reduce fiber content** (∴ and weight) without compromises in the properties

**Or**

Increased **properties** of the composite with no compromises in the density

**Light-weight SMC parts:**

- Lower density
  - Or
- Smaller thickness
INTRODUCING CNC TO THE EPOXY MATRIX

<table>
<thead>
<tr>
<th></th>
<th>( \rho ) (g/cm³)</th>
<th>( E ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>1.15</td>
<td>3.0±0.3</td>
</tr>
<tr>
<td>1.4CNC-epoxy</td>
<td>1.15</td>
<td>4.4±0.5</td>
</tr>
<tr>
<td>2CNC-epoxy</td>
<td>1.15</td>
<td>4.7±0.3</td>
</tr>
</tbody>
</table>

Using the CNC-epoxy matrix, how much fibers can be reduced without compromising the specific properties compared to a composite with neat epoxy?

\[ E_{\text{Composite}} = \frac{3}{8}E_{11} + \frac{5}{8}E_{22} \]

\[ E_{11} = E_m \left(1 + 2 \frac{l_f}{d_f} \eta_L \nu_f \right) \quad ; \quad E_{22} = E_m \left(1 + 2 \eta_L \nu_f \right) \]

\[ \eta_L = \frac{\left( \frac{E_f}{E_m} - 1 \right)}{\left( \frac{E_f}{E_m} + 2 \frac{l_f}{d_f} \right)} \]

\[ \eta_T = \frac{\left( \frac{E_f}{E_m} - 1 \right)}{\left( \frac{E_f}{E_m} + 2 \right)} \]

\[ \Rightarrow \text{Predict fiber contents for CNC-epoxy composites with same specific modulus as composites with neat epoxy and a fiber content of 60% (maximum fiber content)} \]
Determinations of maximum fiber content

- Almost no performance improvement above 60 wt% fiber content
- Found 60 wt% as maximum fiber content with a good fiber wetting
# LIGHT-WEIGHT COMPOSITES WITH CNC

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{theor}}$ (GPa)</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$E_{\text{specific, theor}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60GF/epoxy</td>
<td>14.38</td>
<td>1.71</td>
<td>8.40</td>
</tr>
<tr>
<td>48GF/0.9CNC-epoxy</td>
<td>13.23</td>
<td>1.56</td>
<td>8.48</td>
</tr>
<tr>
<td>44GF/1.1CNC-epoxy</td>
<td>12.73</td>
<td>1.51</td>
<td>8.41</td>
</tr>
<tr>
<td>60BF/epoxy</td>
<td>14.99</td>
<td>1.76</td>
<td>8.48</td>
</tr>
<tr>
<td>48BF/0.9CNC-epoxy</td>
<td>13.41</td>
<td>1.58</td>
<td>8.47</td>
</tr>
<tr>
<td>44BF/1.1CNC-epoxy</td>
<td>13.17</td>
<td>1.54</td>
<td>8.52</td>
</tr>
</tbody>
</table>

* 1.4 wt% CNC in the epoxy
** 2 wt% CNC in the epoxy
DENSITY AND VOID CONTENTS OF THE LIGHT-WEIGHT SMC COMPOSITES

<table>
<thead>
<tr>
<th></th>
<th>( \rho_{c,\text{theoretical}} ) (g/cm(^3))</th>
<th>( \rho_{\text{exp,wd}} ) (g/cm(^3))</th>
<th>Fiber content (acid digestion)</th>
<th>( \rho_{\text{exp,ad}} ) (g/cm(^3))</th>
<th>Void content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60GF/epoxy</td>
<td>1.71</td>
<td>1.67±0.06</td>
<td>0.69±0.08</td>
<td>1.85±0.07</td>
<td>9</td>
</tr>
<tr>
<td>60GF/0.6CNC-epoxy*</td>
<td>1.71</td>
<td>1.74±0.06</td>
<td>0.66±0.05</td>
<td>1.80±0.08</td>
<td>3</td>
</tr>
<tr>
<td>48GF/0.9CNC-epoxy*</td>
<td>1.56</td>
<td>1.51±0.03</td>
<td>0.56±0.05</td>
<td>1.66±0.06</td>
<td>9</td>
</tr>
<tr>
<td>44GF/1.1CNC-epoxy**</td>
<td>1.51</td>
<td>1.49±0.05</td>
<td>0.52±0.06</td>
<td>1.61±0.07</td>
<td>8</td>
</tr>
<tr>
<td>60BF/epoxy</td>
<td>1.77</td>
<td>1.75±0.07</td>
<td>0.72±0.03</td>
<td>1.97±0.07</td>
<td>12</td>
</tr>
<tr>
<td>60BF/0.6CNC-epoxy*</td>
<td>1.77</td>
<td>1.73±0.05</td>
<td>0.71±0.08</td>
<td>1.96±0.1</td>
<td>13</td>
</tr>
<tr>
<td>48BF/0.9CNC-epoxy*</td>
<td>1.59</td>
<td>1.48±0.05</td>
<td>0.55±0.05</td>
<td>1.69±0.07</td>
<td>14</td>
</tr>
<tr>
<td>44BF/1.1CNC-epoxy**</td>
<td>1.55</td>
<td>1.39±0.06</td>
<td>0.53±0.08</td>
<td>1.66±0.1</td>
<td>19</td>
</tr>
</tbody>
</table>

* 1.4 wt% CNC in the epoxy
** 2 wt% CNC in the epoxy
SPECIFIC PROPERTIES OF THE LIGHT-WEIGHTING COMPOSITES

(a) Specific tensile properties \( \times (g/cm^3)^{-1} \)

(b) Specific flexural properties \( \times (g/cm^3)^{-1} \)

(c) Specific impact energy, kJ/m

Fiber-CNC content (wt %)
FRACTURE SURFACE MORPHOLOGY – GF/EPOXY WITH AND WITHOUT CNC

GF60/epoxy

60GF/0.6CNC-epoxy
Contact Angles between Fiber and 2CNC-epoxy matrix:

<table>
<thead>
<tr>
<th></th>
<th>BF</th>
<th>GF</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.7</td>
<td>36.4</td>
<td></td>
</tr>
</tbody>
</table>
Lightweighting Results

Strain at Break (%)

Strength (MPa)

Modulus (GPa)

Impact energy ($\times 10^3$ J/m$^2$)

Tensile properties  Flexural properties

25GF-CNC0  35GF-CNC0  25GF-CNC1.5  25GF-CNC1

Impact energy ($\times 10^3$ J/m$^2$)

25GF-CNC0  25GF-CNC1  25GF-CNC1.5  35GF-CNC0

CREATING THE NEXT®
Presence of 1 wt% CNC increases mechanical performance of SMC with 44-48 wt% to the level of SMC with maximum fiber content → 11% weight reduction

SMC with BF and CNC/epoxy matrix did not meet the properties of BF60/epoxy SMC composites due to high void content and lower wettability.
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