Pultrusion of Fast-Gel Thermoset Polyurethanes: Processing Considerations and Mechanical Properties

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Pultrusion of Fast-Gel Thermoset Polyurethanes: Processing Considerations and Mechanical Properties

- Background: the Composites Industry
- Experimental Strategy
  - Processing
  - System Configuration
  - Mechanical Properties
- Results
  - Processing
  - Mechanical Properties
  - Area & Personnel Monitoring
- Conclusions
What is a ‘Composite’?

- **Broad definition:** A combination of two materials that can do things neither could do alone.

- **Working definition:** A strong or stiff ‘reinforcement’ (usually a fiber) that provides key mechanical properties to a ‘matrix’ (usually a resin) that in turn protects the fiber from stresses and environmental damage.
The Working Definition Covers a Huge Range of Products
U.S. Annual Composites Output
(Year 2000)

$24 Billion
3.9 Billion Pounds
(Resin & Fiber)

Worldwide Annual Output is Estimated at 2.5 Times US (10 Billion Pounds)

Resin Consumption Accounts for 65% of Volume
(2.5 Billion Pounds US / 6.5 Billion Pounds Worldwide)

Source: Composites Fabricators Association
Historic Composites Market Growth
Composites Production by Market Segment - 2001

Market Statistics:

- Transportation: 32%
- Aircraft: 1%
- Construction: 20%
- Corrosion: 11%
- Marine: 11%
- Electrical: 10%
- Consumer: 7%
- Other: 3%
- Appliance: 5%

Source: Composites Fabricators Association
Composites Volume by Molding Process

- Open Molding: 47%
- RTM / VIP: 13%
- Filament Winding: 12%
- Compress. Molding: 18%
- Other RP Processes: 5%
- Pultrusion: 5%

Source: Composites Fabricators Association
Market Statistics:

Composites Volume by Company Size
(Number of Employees)

Large: > 500
Intermediate: 499 >> 20
Owner Operated: < 19

Source: Composites Fabricators Association
Market Statistics:

Market Share by Size

- 50 Large Companies Produce 35%
- 1,200 Intermediate Companies Produce 50%
- 4,200 Small Companies Produce 15%

Source: Composites Fabricators Association
Experimental Procedure

- Identification of candidate polyols, isocyanates, catalysts and mold releases

- Two-phase evaluation of processing characteristics
  - Phase One: Identification of workable chemistries
  - Phase Two: Exploration of temperature & speed envelopes, stoichiometry & mold releases

- Parallel environmental & workplace safety evaluation

- Mechanical properties characterization
Pultrusion System Configuration (Standard)

- PTI Pulstar 804 commercial pultrusion machine
  - Digital control/instrumentation update
  - Pull force instrumentation
  - Real-time data collection to computer

- Coupon die: 25 mm x 3 mm cross-section, 90 cm long
  - Die entrance cooling

- Six independent resistance heaters in 3 heat zones
  - Closed-loop temperature control
  - Real-time data collection

- Conventional ‘bookshelf’ creel and dry fiber guides
  - 32 ends of 366-AD-113 (Type 30 4400-tex) glass fiber
PTI Pulstar 804 Pultrusion Machine

THE UNIVERSITY OF MISSISSIPPI
SCHOOL OF ENGINEERING
COMPOSITE MATERIALS LABORATORY
Six independent resistance heaters in 3 zones with closed-loop controllers.

Die entrance cooling (continuous flow tap water)

90 cm die length

25 mm air gap

Six independent resistance heaters in 3 zones with closed-loop controllers
Pultrusion System Configuration
(Changes for Polyurethane)

- Resin injection/fiber wetting chamber
  - Machined from HDPE
  - Bolted/sealed to die entrance face

- Resin metering and mixing:
  - Commercial meter/mix gear pump system (truck-bed-liner spray equipment)
  - Air-actuated mix head with 30-element disposable static mixer
Entrance plate to reduce resin loss
Length: 30 cm
Exit matches shape and area of die entrance
Entrance/Exit area ratio = 6:1
30-element disposable static mixer

Air-actuated self-purge resin mixhead

Digital gear pumps control component ratio and flow rate independently

Continuous precision ratio control

Built-in reservoirs or pump from drums

Disposable tube connects injection chamber to static mixer
Mechanical Properties Characterization

- Phase One: Screening materials for viability using resin-influenced and resin-dominated properties
  - ASTM D 790  Flexural Properties
  - ASTM D 2344 Short-Beam Shear Strength

- Phase Two: Comprehensive property characterization to identify unexpected strengths and weaknesses
  - ASTM D 790 and 2344, plus...
  - ASTM D 792 Density & Specific Gravity
  - ASTM D 3039 Tensile Strength, Elongation & Modulus
  - ASTM D 695 Compressive Strength
  - ASTM D 4812 & ISO 179 Impact
  - ASTM D 785A Rockwell Hardness
  - ASTM D 648 Heat Deflection Temperature
  - Bayer “Method A” Paint Adhesion
Phase One Mechanical Properties
Test Protocol

- ASTM D 790 - Flexural strength testing used for near real-time screening
  - Fast sample preparation
  - Samples post-cured 45 min @ 120°C
  - Ultimate strength and elongation to failure data used

- ASTM D 2344 - Short-beam shear strength test used for final resin system selection
  - Longer sample prep cycle needed
  - Room temperature aging
  - Resin-dominated property – best discriminator
Results

- Processing
- Mechanical Properties
- Area & Personnel Monitoring
Processing Results

- High speeds (120-150 cm/min) with low pull forces were achieved with little or no difficulty
  - No deterioration of mechanicals with speed
  - Upper speed limit is undetermined
- Organo-phosphate/organic ester mold releases produced excellent, glossy finish
- Resin is forgiving and ‘heat-loving’
  - Only one system ‘crash’ – chemistry modified for Phase Two
  - Benign response to extreme speed & temperature changes
  - Increased center zone temperature improved quality
- Problems encountered on long-term stability test runs
  - Solutions have been developed but not yet tested
Entrance Cooling Water - ON

Temperature Settings:

- Zone 1: T & B, No Heat
- Zone 2: T & B, 235°C
- Zone 3: T & B, 125°C

Typical temperature zone settings
High Temperature of Center Zone Migrated into Entry & Exit Zones

Temperature Change over Time

Time of Day

Temperature (C)

Entry Zone
Exit Zone
Increased Temperature in Entry Zone Caused Wetout to Deteriorate

Wetout deterioration affected mechanical properties, and could be readily seen as the part exited the die.

**Graph:**
- **Title:** ASTM D 790 Flex Strength
- **Y-axis:** ksi
- **X-axis:** Good Wetout, Poor Wetout
- **Data Points:**
  - Good Wetout: 250 ksi
  - Poor Wetout: 150 ksi
Optimized Injector/Die Design Should Prolong Wetout Time

- Entrance Cooling
- Zone 1: T & B 230°C
- Zone 2: T & B 125°C
- Possible Exit Cooling
Two resin systems tested in Phase Two:

- Baydur STR 2000 (1:1 by Volume System)
- Baydur STR 3000 (Standard System)
## Physical and Mechanical Properties

<table>
<thead>
<tr>
<th>Property (Units)</th>
<th>Test Method ASTM (Other)</th>
<th>Baydur STR 2000</th>
<th>Baydur STR 3000</th>
</tr>
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<tbody>
<tr>
<td>Specific Gravity (@23°C)</td>
<td>D 792</td>
<td>2.07</td>
<td>2.10</td>
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<tr>
<td>Rockwell Hardness (R)</td>
<td>D 785 A</td>
<td>122</td>
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<td>Tensile Strength (G-Pa)</td>
<td>D 3039</td>
<td>&gt; 1.34</td>
<td>&gt; 1.34</td>
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<td>Compressive Strength (M-Pa)</td>
<td>D 695-96</td>
<td>374</td>
<td>404</td>
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<td>Short Beam Shear (M-Pa)</td>
<td>D 2344</td>
<td>74</td>
<td>80</td>
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<td>Short Beam Shear (M-Pa)</td>
<td>D 2344</td>
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<td>17</td>
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<tr>
<td>Transverse to Fiber Direction</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Property (Units)</td>
<td>Test Method ASTM(Other)</td>
<td>Baydur STR 2000</td>
<td>Baydur STR 3000</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>-------------------------</td>
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<tr>
<td>Flexural Strength (M-Pa)</td>
<td>D 790</td>
<td>1400</td>
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<td>Flexural Modulus (G-Pa)</td>
<td>D 790</td>
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<td>Flexural Strain (%)</td>
<td>D 790</td>
<td>3.0</td>
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<td>Charpy Impact (K-J/m²)</td>
<td>(ISO 179)</td>
<td>&gt;189</td>
<td>&gt;189</td>
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<tr>
<td>Un-notched Beam Impact (K-J/m)</td>
<td>D 4812</td>
<td>2.9</td>
<td>3.1</td>
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<tr>
<td>HDT @1820 kPa (°C)</td>
<td>D 648</td>
<td>240</td>
<td>&gt;250</td>
</tr>
</tbody>
</table>
Ease of Fastener Attachment

Example of self-tapping screws in vinyl ester, polyurethane, and polyester pultruded parts

No splitting of the part is seen with polyurethane
Results of Bayer ‘Method A’ Paint Adhesion Testing

- Method similar to ASTM D 3359

- Sample preparation:
  - Part painted with commercially-available 2-part acrylic-polyurethane automotive finish
  - Cured 4 days at room temperature
  - Scratched through to substrate to create 100 squares

- Pressure-sensitive tape applied & pulled off parallel to surface

- Both systems showed 0% loss
Pultrusion - Incorporation of Mat and Veil

- Baydur STR 3000 Successfully Processed
  - Bar 6.4 cm wide (2.5 inch)
  - Roving core, mat and veil on each face (64 wt% glass)
- Multiple Injection Points to Distribute Resin
- Injector acts as last 2 or 3 forming guides
## Short-Beam Shear with 6.4 cm Bar Incorporating Mat and Veil

<table>
<thead>
<tr>
<th>Property (Units)</th>
<th>Test Method</th>
<th>Baydur STR 300</th>
</tr>
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<tbody>
<tr>
<td>Short Beam Shear (M-Pa)</td>
<td>D 2344</td>
<td>53</td>
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<tr>
<td>Short Beam Shear (M-Pa) Transverse to Fiber Direction</td>
<td>D 2344</td>
<td>31</td>
</tr>
</tbody>
</table>
Area & Personnel Monitoring: Criteria

- Testing conducted during Phase Two trials
- Objective: determine airborne concentrations of MDI in breathing zone of machine operators and in the work area

- Permissible Levels:
  - ACGIH Threshold Limit Value (TLV/TWA)
    - 5 parts per billion (ppb) averaged over 8-hour workday
  - OSHA Permissible Exposure Limit (PEL-C)
    - 20 parts per billion (ppb) should not be exceeded during any part of the day
Area & Personnel Monitoring: Results

- Sampling Method: modified OSHA 47

- Testing protocol
  - Ten samples from breathing zones of 3 operators
  - Twenty-five samples from 5 locations around the pultrusion machine

- Results:
  - Breathing zone samples were well below TLV values (0.2 ppb to non-detectable)
  - Area samples, placed around pultrusion machine, ranged from 18 ppb (at die exit, under vent hood) to undetectable
Conclusions

- Two-part polyurethane resins appear to be a very promising alternative to currently used materials
  - Superior mechanical properties
  - High productivity potential
  - Relatively easy processing
  - Controllable workplace environment
- Further testing required to establish range of suitable applications
  - Workplace exposure
  - Chemical compatibility
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Spray-Up

Fiber is chopped into short filaments, combined with resin in a ‘chopper gun’ and sprayed into a mold. Resin cures at room temperature. Used to make pleasure boats, bathtubs and shower enclosures, other similar structures.
Wet Lay-up
Prepreg Manufacture

Resin Film Pre-Cast onto Paper

Resin Film & Fiber Combined

Reverse Roller Or Doctor Blade

Precision Nip Rollers
Prepreg Lay-up

- Prepreg layers
- Autoclave
- Oven
Filament Winding

Fiber is pulled through resin, then wound around a mandrel in a computer-controlled pattern. After winding, the part is usually cured in an oven. Used to make tanks & pressure vessels.
Fiber is wetted with resin and pulled through a heated die where the resin solidifies. Used to make 2-D shapes such as window & door components.
Fiber pack is placed into mold, mold is closed and resin is injected. Resin cures with heat from mold. Mold is opened and finished part removed. Used to make many high-performance 3-D parts for cars, trucks, aircraft, & personal watercraft.