Improving the Performance of Epoxy Syntactic Foams: Part 1 - Curatives

Evonik Corporation / Dixie Chemical Joint Webinar Series

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Introduction

• Expanding deepwater exploration requires longer reach-out distances (>30 mi)
• Extended pipe lengths exposed to higher subsea oil temperatures
• Greater requirements for insulation
  • Pipe-in-pipe
  • Flexible insulated pipe
  • Wet insulated pipe => syntactic foam

Source: Gary Gladysz
Research goals

- Part 1 - Investigate the potential of monoanhydride/dianhydride blends as thermal curatives for epoxy-based syntactic foams
- Part 2 - Conduct a detailed testing program using optimized curative blends to model in-service performance
- Part 3 - Fabricate parts for deep sea installation and real-time monitoring

Source: Gary Gladysz
Syntactic foam is a novel insulating technology

**What is it**
- Closed cell foam material
- Hollow glass or ceramic microspheres in binder (pure syntactic)
- Hollow macrospheres & microspheres in binder (composite syntactic)

**How is it used**
- Buoyancy for drill risers, deep sea vehicles
- Thermal insulation of deep sea piping, manifolds

**What are the benefits**
- Lightweight, buoyant, low water uptake, high hydrostatic strength
- Maintains internal pipe temperatures, ensures continuous flow
- Reduces paraffin formation on pipe walls

Sources:
http://www.afglobalcorp.com/products-and-services/production/insulation
## Critical factors for syntactic foam performance

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Property</th>
<th>Function of</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight</td>
<td>Density (buoyancy)</td>
<td>Sphere wall thickness and volume %</td>
</tr>
<tr>
<td>Hydrostatic pressure</td>
<td>Compressive strength</td>
<td>Binder rigidity, sphere wall thickness and volume %</td>
</tr>
<tr>
<td>Insulation</td>
<td>Thermal conductivity</td>
<td>Sphere wall thickness and volume %</td>
</tr>
<tr>
<td>Heat</td>
<td>Glass transition temperature</td>
<td>Binder selection (dispersed phase)</td>
</tr>
<tr>
<td></td>
<td>Heat capacity</td>
<td>Volume of solids (glass and binder)</td>
</tr>
<tr>
<td>Integrity</td>
<td>Crack resistance</td>
<td>Binder flexibility, adhesion to spheres</td>
</tr>
<tr>
<td></td>
<td>Water absorption</td>
<td>Binder selection (hydrostatic strain)</td>
</tr>
</tbody>
</table>

Glass microsphere

Source: Gary Gladysz
Epoxy syntactic foams are the workhorse

- Most versatile alternative to polypropylene, polyurethane, silicone
- Track record based on standard DGEBA chemistry
- Multiple epoxy curatives for ambient or thermal cure
- Typically monoahydride blends – flexible DDSA with rigid MTHPA

![Chemical structures of DDSA and MTHPA](image)
Driving performance with curatives

- Anhydrides include monoanhydrides and dianhydrides
- Liquid monoanhydrides are frequently favored in epoxy formulations for ease of mixing and metering
  - NADIC® Methyl anhydride
- Solid dianhydrides impart a superior mix of performance properties including high thermal stability
  - Benzophenone tetracarboxylic dianhydride (BTDA®)
- Blends of dianhydrides in monoanhydrides facilitate mixing and allow incorporation of micro- and macrospheres
Blended curatives are the gateway

- New solutions required
  - Farther offshore
  - Deeper (higher hydrostatic pressures)
  - Higher crude temperature
- Opportunity to explore the benefits of blends with BTDA as a new class of thermal curative
Blends greatly influence processing, properties

Notes:

- All tests with EPON 826
- 2-Ethyl-4-methylimidazole @ 0.2 phr
- Cured 4 hr @ 200°C
- Viscosity, cP x 10E3 @ 50°C
- Flexural strength, psi x 10E3
Initial data

Relation: hydrostatic and uniaxial compression strength (epoxy-based syntactic foams)

<table>
<thead>
<tr>
<th>Syntactic foam components</th>
<th>Formulation</th>
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<tbody>
<tr>
<td>DGEBA</td>
<td>45%</td>
</tr>
<tr>
<td>BDTA</td>
<td>14%</td>
</tr>
<tr>
<td>NMA</td>
<td>20%</td>
</tr>
<tr>
<td>BDMA</td>
<td>1%</td>
</tr>
<tr>
<td>Microballoons (SG=0.23)</td>
<td>20%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive Strength, MPa</td>
<td>104</td>
</tr>
<tr>
<td>Glass transition temperature, °C</td>
<td>232</td>
</tr>
</tbody>
</table>

Source: Gary Gladysz personal data, UAB data
Future formulation and testing needs

• Further optimization via comparative study of
  – Epoxy systems of differing chemistries
  – Microspheres of varying composition, wall thickness and particle size
  – Detailed property investigation (density, compression, flexure, conductivity, glass transition, heat capacity, water ingress)

• Study of comparative syntactic foam formulations in service

• Modeling systems in order to improve design/performance
Conclusions

1. Syntactic foams represent a key technology for deep sea exploration of oil and gas resources.

2. The full benefit of performance properties can be achieved by carefully formulating epoxy systems.

3. Epoxy thermal curatives play a significant role.

4. Expanded choices of curative blends allow tailoring properties to address harsher offshore O&G environments.

5. Modeling is necessary to predict performance and improve design of formulations.
Acknowledgements

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Thanks kindly for your attention!