Degradation of Carbon Fiber Composite Facings and Sandwich Materials with Polymeric Foam Core Due to Sea Environment

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Objective: To evaluate the combined effects of harsh naval environment (sea water and low temperature) on the mechanical properties of carbon fiber and vinyl ester resin based polymeric composites and sandwich structures.

Undamaged PVC foams and sea-water induced damage in same foam materials
Myth Behind Moisture Uptake Curves

- Schematic curves representing four categories of recorded non-fickian weight-gain sorption (data in *Polymers and Polymeric Composites*). The solid line, designated by LF, corresponds to linear Fickian diffusion. “A” and “B” couple diffusion with visco-elasticity. “C” corresponds to growing damage. “D” accounts for leaching and slow chemical reaction.
- Sorption process depends on material and severity of exposure conditions.
- Cases “LF”, “A”, and “B” are reversible, cases “C” and “D” are irreversible.
Typical “hysteresis loops” for sorption, desorption, and re-sorption weight gain and weight loss data, can be modeled by a combined diffusion/capillary-action analysis.

Compressive strain measurement of sea water saturated carbon fiber-vinyl ester composite facing during drying.
Improved Moisture Uptake Measurements with Larger Sample Size

Over 45 hours, weight gain of 0.065% at RH 80%

<table>
<thead>
<tr>
<th>CFVE type</th>
<th>Average coefficient of moisture expansion (με/1% weight gain)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[0/90]$_{2S}$</td>
<td>340</td>
</tr>
<tr>
<td>[15/75]$_{2S}$</td>
<td>730</td>
</tr>
<tr>
<td>[30/60]$_{2S}$</td>
<td>760</td>
</tr>
<tr>
<td>[±45]$_{2S}$</td>
<td>1020</td>
</tr>
</tbody>
</table>
In-plane sea-water induced expansion to predict dimensional changes and corresponding mechanical stresses. Developed a predictive shear-lag model to evaluate the resulting structural shape distortions.

Fig. 1: Configuration for tensile loading on bottom facing “3”. Regions “1” and “2” are top facing and foam core, respectively.

\[ \alpha^2 = \frac{2G}{hHE} \]

Model Prediction: Ratio of Strain at the center for top facing to bottom facing was predicted to be 0.09 while the laboratory data indicated it to be 0.10
Sandwich Materials: Carbon-VE sandwich panel: 0/90 balanced/symmetric (T700/Diab H100/Derakane 510A-40: skin, t= 1.3 mm (0.05”), Post-cured@180F/8 hours)
Sandwich Material preparation and testing

• PVC closed cell H100 foam sample
• Carbon fiber vinyl/ester sample with dimension of 200 mm by 25 mm
• Sandwich structure sample with dimension of 200 mm by 25 mm
• Precondition: immersed in simulated sea water at 40°C at least 3 month
High Resolution X-Ray Computer Tomography for Micro-Structure

Collaborations with Helmholtz Zentrum – Berlin, Germany
High Resolution XCT Result for Sandwich Composite Material

Foam Core Cell Variation (H100)

Interface Strongly Affected By Sea Water Exposure Showing Large Reduction in Debond Energy Release Rate

Carbon Composite Facing Material (T700)
3-D Tomography of Sandwich Structure
Z-Frames

6-45-N-13: Lower Velocity Impact: 194 meters/sec
Experiments

- Polymeric H100 foam
  - Tensile test: Strain rate 0.5 mm/min, up to 0.6 MPa
  - Torsion test: Rate of 10 degree/min within range of $-5^\circ \leq \theta \leq 5^\circ$
- Carbon vinyl/ester facing composites
  - Young’s modulus $[\pm45]_{2s}$ and $[0/90]_{2s}$
  - Failure strength
- Sandwich structure
  - Foam/facing interface fracture toughness: Strain rate of 2 mm/min
Foam Experimental setup

- Polymeric H100 foam (Young’s and shear modulus)
  - Tensile test: Loading rate 0.5 mm/min, up to 0.6 MPa
  - Torsion test: Rate of 10 degree/min within range of $-5^\circ \leq \theta \leq 5^\circ$
• Equilibrium weight gain of different thicknesses using 4, 8, and 12 mm thick samples of same geometry was proportional to the ratio of surface area/volume. This is yet another verification of the fact that water ingress is confined to an outer boundary layer.
Core material preparation and testing

- PVC closed cell H100 foam (100 kg/m³) by DIAB
- Precondition: Soaking in simulated sea water at 40°C at least 2 months
Through Tickness Variation of H 100 Foam Core

A Maximum Variation in E of 12% Observed in Dry Foam Depending on 4mm Thick Sample Location

<table>
<thead>
<tr>
<th>Sample layer</th>
<th>AI</th>
<th>AII</th>
<th>BI</th>
<th>BII</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67.33</td>
<td>67.74</td>
<td>67.55</td>
<td>65.35</td>
</tr>
<tr>
<td>2</td>
<td>71.51</td>
<td>72.24</td>
<td>72.86</td>
<td>69.54</td>
</tr>
<tr>
<td>3</td>
<td>72.15</td>
<td>73.55</td>
<td>72.39</td>
<td>72.21</td>
</tr>
<tr>
<td>4</td>
<td>69.25</td>
<td>70.21</td>
<td>69.57</td>
<td>69.98</td>
</tr>
<tr>
<td>5</td>
<td>68.69</td>
<td>69.39</td>
<td>69.83</td>
<td>68.89</td>
</tr>
</tbody>
</table>
PVC foam: Young’s modulus

- Dry foam sample: After 2 and 6 weeks at -5 °C, exposure to low temperature does not significantly affect the value of E for specimens.
- Wet foam samples: Tested before/after soaking in sea water (10 weeks) and retested at -5 °C. It showed approximately 5% degradation.
Evaluation of Wet Moduli & Need for Torsion

Example:

\[ G_{\text{dry}} = 26 \text{ MPa}, \quad G_{\text{wet}} = 20 \text{ MPa}, \quad \delta \sim 0.15 \text{ mm} \]

Analysis as shown above yields a Shear modulus for the foam in the wet core region showing a significant reduction of ~ 70% when compared to dry state of the foam.
PVC foam: Shear modulus

- Dry foam sample:
  - At room, $G \sim 23.3 \text{ MPa} \leq G \leq 28.9 \text{ MPa}$
- Wet foam samples:
  - 5% degradation after soaking in sea water over 2 months
  - 7% reduction after keeping in a freezer at $-5 \, ^\circ\text{C}$ for additional 5 weeks. This corresponds to estimated degradation of shear modulus in the saturated region by up to 50% corresponding to of 0.2-0.45 mm.
PVC foam: Failure strength

- Failure stress of PVC foam is approximately 2.5 MPa. Sea water could degrade the $\sigma_{\text{failure}}$ up to 10% and combined effect of sea water and low temperature slightly degrades $\sigma_{\text{failure}}$. 

![Graph showing stress-strain relationship for dry and wet samples at different temperatures.](image)
Composite Facing Experimental setup

- Carbon fiber vinyl/ester facing composites
- Young’s modulus \([\pm 45]_2s\) and \([0/90]_2s\) at 300 \(\mu\varepsilon/\text{min}\)
- Failure strength

3 cycles of load/unload
Typical material properties of carbon fiber vinyl/ester composites

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitudinal modulus $[0/90]_{2s}$</td>
<td>80</td>
<td>GPa</td>
</tr>
<tr>
<td>Longitudinal modulus $[\pm 45]_{2s}$</td>
<td>15</td>
<td>GPa</td>
</tr>
<tr>
<td>Ultimate strength $[0/90]_{2s}$</td>
<td>450</td>
<td>MPa</td>
</tr>
<tr>
<td>Ultimate strength $[\pm 45]_{2s}$</td>
<td>120</td>
<td>MPa</td>
</tr>
</tbody>
</table>
Carbon facing: Young’s modulus

- Dry facing: Young’s modulus $[\pm 45]_2s$ and $[0/90]_2s$ yielded 15 GPa and 80 GPa respectively.
- Wet facing:
  - Pre-soaking in sea water at least 3 months: No significant degradation in modulus of $[\pm 45]_2s$
  - Subsequently kept in freeze at -10 °C for 2 weeks, testing them at room, 0, and -15 °C as shown in Fig, 5% increase of $E$ was found.
Carbon facings: Failure strength

- $\sigma_{\text{failure}}$ data of $[\pm45]_{2s}$ yielded approximately 130 MPa and no difference due to low temperature, but $\sigma_{\text{failure}}$ of $[\pm45]_{2s}$ decreases by 5% due to sea water effect.
Fatigue Behavior of $[\pm 45]_2s$ Carbon Fiber Vinyl Ester Facing Material Due To Sea Environment

- Frequency of 1 HZ
- $\sigma_{\text{min}}/\sigma_{\text{max}} = 0.2$ with $\sigma_{\text{max}}$ of 80 MPa
Comparison of dry and wet immersed samples

Number of cycles to failure of $[\pm 45]_{2s}$ samples under cyclic loading at 1 Hz frequency
Comparison of dry and wet one sided immersed samples

Number of cycles to failure of $[\pm 45]_{2s}$ samples under cyclic loading at 1 Hz frequency
# Cyclic Fatigue Results on Composite Facing Materials

<table>
<thead>
<tr>
<th>Condition</th>
<th>Cyclic Fatigue Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry in air</td>
<td>Reference State</td>
</tr>
<tr>
<td>Wet in air</td>
<td>30.1 %</td>
</tr>
<tr>
<td>Dry immersed</td>
<td></td>
</tr>
<tr>
<td>(All sides of sample surrounded</td>
<td>71.8 %</td>
</tr>
<tr>
<td>by water under fatigue stress)</td>
<td></td>
</tr>
<tr>
<td>Wet immersed</td>
<td>84.5 %</td>
</tr>
<tr>
<td>Dry one side of facing immersed</td>
<td>42.7 %</td>
</tr>
<tr>
<td>Wet one side of facing immersed</td>
<td>47.3 %</td>
</tr>
</tbody>
</table>
A single edge crack oriented at 45° degrees to the load direction, such as in dry fatigue.
The same crack as in previous slide but with internal pressure $p$ activated during the downloading stage of the fatigue cycle, such as occurs under immersed fatigue.
X-racy CT Results for **Unconfined** Dry Specimens after Fatigue Failure

Away from Failure

Midway of the Failed Specimen

Near Failure Zone
X-racy CT Results for Water Confined & Wet Samples after Fatigue Failure

- Near Grip
- Away from Failure
- Middle of the Specimen
- Near Failure Zone
Foam/facing interface fracture toughness

Delamination setup in a cold chamber

\[
G_c = \frac{1}{b} \cdot \frac{\Delta U}{\Delta a}
\]

\(\Delta U\) is the area under the load-displacement trace as the crack grows;

\(\Delta a\) is the extended crack length recorded during the test, and \(b\) is the width of specimen.

The value calculated is the average energy consumed for the crack extension \(\Delta a\).

• Sandwich specimens were cut and machined to dimensions of 250 mm in length, 25 mm in width and 25 mm in thickness.

• The specimens were placed an inside environmental chamber, within which was encased a custom made fixture attached to 250 lb tensile load cell to perform delamination tests as shown in the Figure.

• Programmed loads were monotonically increased under displacement control until noting an abrupt drop in their amplitudes, at which stage crack extensions were observed and the machine unloaded back to zero displacement.

• This procedure was repeated until delaminations approached the far edge of a specimen.
Typical interfacial fracture tests

Load (N) vs. Displacement (mm) graph showing the load at different displacements with annotations for each crack and a doubtful loop.
Delamination Crack Morphology

Dry Sample

Sea Water Soaked Sample
Foam/facing interface fracture toughness

<table>
<thead>
<tr>
<th>Condition (No of samples)</th>
<th>$G_c$ (Front) (N/m²)</th>
<th>$G_c$ (Back) (N/m²)</th>
<th>% Avg. Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry (&gt; 15)</td>
<td>580-952</td>
<td>541-963</td>
<td></td>
</tr>
<tr>
<td>Wet (10)</td>
<td>432-619</td>
<td>451-632</td>
<td>30%</td>
</tr>
<tr>
<td>Cyclic wet frozen (5)</td>
<td>405-690</td>
<td>420-620</td>
<td>Similar to sea effect</td>
</tr>
</tbody>
</table>
Sea Water and Temperature Effects on Single Carbon Fibers

Objective: Observe sea water degradation effects on the properties of sized carbon fibers.

Method: A nano-tensile testing system (Figure 1) was used to apply simultaneous dynamic and monotonic loading to determine instantaneous dynamic modulus as a function of global displacement/strain. Environmental degradation is presented as a decrease in storage modulus with increased exposure time in sea water at elevated temperatures (Figure 2).

Results: Little knowledge exists on the effect of sea environment on the mechanical properties of individual carbon fibers. Current work, aided by precision instrumentation of nano-indenter load cell, has demonstrated a degradation of mechanical stiffness with time and elevated temperature of sea water exposure. Figure 2 highlights the trend of instantaneous modulus reduction at 40, 60, and 80°C for two month exposure to sea water.

Current Research: Long term exposure conditioned samples are being prepared to determine similar effects over months and years of exposure. Exploration of sea water exposure on ultimate failure strength will also be explored, and coupled with possible description of loss mechanisms.

Navy Relevance: Marine composites are exposed to sea water environment over extended periods. Sea water induced degradation of mechanical response of single carbon fiber should be carefully evaluated for naval applications.
End-notch Crack Effect on Fibers soaked for 49 days in sea water

CF tow

Sea water vile

Mechanical Degradation

Storage Modulus (GPa)

Ambient and Aged

60 °C

80 °C

Mechanical Degradation

Notched

Un-notched

Failure of Samples

Stress (MPa)

Strain

Failure of Samples

Strain
Sea Water Effect on CF Surface Implications to Interface Shear Strength

Ambient (60kx) 4 month at 80C (50kx)
Multi Modality

1 mm
Imaging with Neutrons - New Research Field

- Hydrogen
- Carbon & Oxygen
- Gadolinium
- Silicon & Aluminum

Try this with X-rays!

\[ I = I_0 e^{-\Sigma x} \]
Concluding Remarks

- The shear and Young’s moduli of polymeric foam were tested by means of novel techniques and found to be $G = 25$ MPa and $E = 60$ MPa, respectively.
- Only the outer boundary of PVC foam core was penetrated and degraded due to the sea water while the inner part still remained dry. No significant reduction could be detected under tensile tests.
- Exposure to sea environment and low temperature resulted in approximate 7% degradation under torsion. This could degrade the shear modulus of the saturated region ($G_w$) by up to 50% corresponding to of 0.2-0.45.
- $\sigma_{\text{failure}}$ of foam core was approximately 2.5 MPa and reduced by up to 10% due to sea environment. No significant reduction was found when combined effects of sea and low temperature environment.
Concluding Remarks

• Young’s modulus of $[\pm 45]_2s$ and $[0/90]_2s$ facing yielded 15 GPa and 80 GPa, respectively. Both were insensitive to coupling effect in term of modulus. However, it was shown that $\sigma_{\text{failure}}$ of $[\pm 45]_2s$ decreased by 5% due to sea water and has slightly reduced further with subsequent freezing after soaking.

• Fatigue life of fiber reinforced composite lay-ups is drastically shorter under immersed conditions. The major effect of water ingress is to enhance delamination growth during the down loading stages of fatigue.

• The above enhancement is caused by the near incompressibility of water as it resists being squeezed out. This resistance induces internal stresses that are several orders of magnitude larger than those due to mechanical loads.

• The interfacial fracture toughness $G_c$ of sandwich lay-up decreased by 30% due to sea environment. The result indicated that only exposure to sea water may severely reduce the interfacial toughness.