Effects of Ultraviolet Surface Treatment on Adhesion Strength of Carbon/Epoxy Composite

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**Motivation**

### Mechanical Design Lab. with Advanced Materials

#### Mechanical joint
- Ease to disassemble
- No surface treatment
- Easy to inspect
- For thick composite

#### Adhesive joint
- Distributed load
- Without hole
- Good fatigue resistance
- High damping
- For thin composite

**Advantage**
- With bolt hole
- Failure of fiber
- Stress concentration
- Heavy weight
- Corrosion

**Disadvantage**
- Difficult to inspect
- Difficult to disassemble
- Careful surface treatment
- Sensitive to environment

To enhance adhesion performance
⇒ Surface treatment of composite materials

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**Surface treatment methods for composite structures**

**Mechanical treatment**
- abrasion
- sand blasting
  ⇒ labor-intensive
  ⇒ improper for clean environment
due to particles

**Chemical treatment**
- plasma, electron / ion beam
- chemical etching
- flame
- ultraviolet
  ⇒ environmentally clean
  ⇒ no need of peripheral devices
  ⇒ inexpensive
  ⇒ easily applicable to manufacturing process
Most of the degradation of polymers takes place from 280nm to 400nm.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylacetate</td>
<td>280</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>300</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>318</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>320</td>
</tr>
<tr>
<td>Polyester</td>
<td>325</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>285 – 305</td>
</tr>
</tbody>
</table>


Ultraviolet chamber design

<table>
<thead>
<tr>
<th>Specification of UV-A and UV-B lamps</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lamp Power (W)</strong>: 40</td>
</tr>
<tr>
<td><strong>UV output (W)</strong>: 7.0</td>
</tr>
<tr>
<td><strong>Lamp current (A)</strong>: 0.43</td>
</tr>
<tr>
<td><strong>Length (mm)</strong>: 1220</td>
</tr>
<tr>
<td><strong>Diameter (mm)</strong>: 38</td>
</tr>
<tr>
<td><strong>Wavelength (nm)</strong>: 315 – 400</td>
</tr>
<tr>
<td><strong>Peak (nm)</strong>: 360</td>
</tr>
<tr>
<td><strong>ASTM D5208, G53</strong></td>
</tr>
</tbody>
</table>

UV-A ⇒ 315 – 400nm
UV-B ⇒ 280 – 315nm
UV-C ⇒ 100 – 280nm
Adhesion test: double lap shear test conditions

- Specimen: carbon/epoxy composite [0]_{10T} (SK chemicals, USN 150)
- UV irradiation: UV-A (315 – 400nm), UV-B (280 – 360nm)
- Adhesive: structural epoxy adhesive (3M, DP460)
- Adhesive layer thickness: 0.1mm
- Adhesive cure condition: 80°C  6atm  2.5hr
- Test equipment: INSTRON 4206 UTM

Adhesion test: double lap shear test results

- Adhesion strength with respect to UV wavelength
  - UV-B treatment > UV-A treatment
  - 90% increase in shear strength
**Adhesion test: double lap shear test results**

- Failure mode transition: interfacial failure $\Rightarrow$ adherend failure

**interfacial failure**

without

UV-B 1hr

UV-B 3hr

UV-B 6hr

**adherend failure**

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**Adhesion test: cleavage peel test conditions**

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**Adhesion test: cleavage peel test results**

- 3 times higher peel strength was obtained (about 4000N/m)
- Excessive UV-B irradiation longer than 12hr
  ⇒ decrease in peel strength due to degradation of adherend

**Introduction to XPS**

- XPS (X-ray Photoelectron Spectroscopy) or ESCA (Electron Spectroscopy for Chemical Analysis)
  ⇒ Application of Einstein’s photoelectric effect
  
  \[ E_b = h\nu - E_k - \phi \]

  - \( E_b \): binding energy of the atomic orbital
  - \( h\nu \): energy of the incident photon
  - \( E_k \): kinetic energy of the emitted electron
  - \( \phi \): work function

  ![Diagram of XPS process]
**Introduction to XPS**

- **Advantages of XPS**
  - Identification of all elements (except H, He) present at concentrations > 0.1 atomic %
  - Quantitative determination of the approximate elemental surface condition
  - Information about the molecular environment (oxidation state, bonding atoms)
  - Identification of organic groups using derivation reactions

- **Applications of XPS**
  - Surface or chemical modification
  - Adhesion
  - Degradation
  - Diffusion

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**Survey spectrum of carbon/epoxy composite**

- X-ray source: Mg-Kα (1253.6eV)
- Power: 120W (12kV, 10mA)
- Pressure: 7x10^-9 Torr
- Take-off angle: 90°
- Major peaks: C1s and O1s
- Minor peaks: N1s, Cl2p

Spectrum analysis (high resolution scan)
**Atomic concentration : carbon/epoxy**

- Specimen : USN 150 carbon/epoxy composite
- UV treatment condition : without, UV-A (6, 12hr), UV-B (6, 12hr)

![Graph showing atomic concentration for carbon/epoxy](image)

**Atomic concentration : epoxy resin**

- Specimen : cured epoxy resin of USN 150 prepreg
- UV treatment condition : without, UV-A (6, 12, 48hr), UV-B (6, 12, 48hr)

![Graph showing atomic concentration for epoxy resin](image)

After UV-B treatment ⇒ oxygen concentration ↑
⇒ chemical structures changed by UV and oxygen in the air (photo-oxidation)
Chemical shift in binding energies of peak points
- Atoms in a high oxidation state ⇒ XPS peaks at high binding energy
- Modification of chemical bond composition on surfaces
- Need to analyze the contents of C–C, C–O, C=O bonds from XPS spectrum

Chemical bond composition
⇒ Calculation of percentage of area below each decomposed curve

Binding energies of chemical bonds for decomposition of $C_{1s}$ spectrum

<table>
<thead>
<tr>
<th>Chemical bond</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C$–$C$/C–$H$</td>
<td>$284.6 \pm 0.1$</td>
</tr>
<tr>
<td>C–O</td>
<td>$286.2 \pm 0.1$</td>
</tr>
<tr>
<td>(C–OH, C–O–C)</td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>$288.5 \pm 0.1$</td>
</tr>
<tr>
<td>(C=O, O=C–OH)</td>
<td></td>
</tr>
</tbody>
</table>

$C_{1s}$ spectrum decomposition: carbon/epoxy

Specimen: USN 150 carbon/epoxy composite
Treatment condition: without, UV-A (6, 12hr), UV-B (6, 12hr)
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**C₁s spectrum decomposition : epoxy resin**

- Specimen: cured epoxy resin of USN 150 prepreg
- Treatment condition: without, UV-A (6, 12, 48hr)

(a) without  
(b) UV-A 6hr  
(c) UV-A 12hr  
(d) UV-A 48hr

Specimen: cured epoxy resin of USN 150 prepreg
Treatment condition: without, UV-B (6, 12, 48hr)

(a) without  
(b) UV-B 6hr  
(c) UV-B 12hr  
(d) UV-B 48hr

C₁s spectrum decomposition: epoxy resin

- C–C/C–H
- C–O
- C=O
Summary of XPS test results

- From adhesion strength
  - UV-B treatment > UV-A treatment
  - Failure mode transition
    Interfacial failure ⇒ adherend failure
- From the results of atomic concentration and C\textsubscript{1s} spectrum decomposition
  - UV-A treatment
    ⇒ little difference in atomic concentrations and chemical bond compositions
  - UV-B treatment
    ⇒ Photo-oxidation
    ⇒ Oxygen concentration ↑, C=O bond composition ↑

Why UV-B treatment was better?

- Wavelengths for dissociation of chemical bonds \(^{(2)}\)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy (kcal/mol)</th>
<th>(\lambda) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>85</td>
<td>336</td>
</tr>
<tr>
<td>C–H</td>
<td>95 – 100</td>
<td>286 – 301</td>
</tr>
<tr>
<td>C–O</td>
<td>80 – 100</td>
<td>286 – 357</td>
</tr>
<tr>
<td>C–Cl</td>
<td>60 – 86</td>
<td>332 – 477</td>
</tr>
<tr>
<td>C=O</td>
<td>160</td>
<td>179</td>
</tr>
</tbody>
</table>

Ref. (2) Photodegradation of polymers, Springer, 1996

- UV-A lamp : 315 – 400nm (peak : 360nm)
- UV-B lamp : 280 – 360nm (peak : 306nm)
  ⇒ covers nearly all wavelengths for bond dissociations
**Why adhesion strengths increased?**

- Dipole moment of chemical bonds (3)
  
<table>
<thead>
<tr>
<th>Bond</th>
<th>( \mu ) (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C, C=C</td>
<td>0</td>
</tr>
<tr>
<td>C–H</td>
<td>0.22</td>
</tr>
<tr>
<td>C–O</td>
<td>0.74</td>
</tr>
<tr>
<td>O–H</td>
<td>1.51</td>
</tr>
<tr>
<td>C=O</td>
<td>2.3 – 2.7</td>
</tr>
</tbody>
</table>

  - C=O: high electronegativity of oxygen and double covalent bond
  - \( \mu \): high dipole moment
  - O–H: high dipole moment and hydrophilicity

1 D (Debye) = 3.336\times10^{-30} \text{ C\cdot m}

Ref. (3) Surfaces, Interfaces, and Colloids, Wiley & Sons, 1999

**UV-B surface treatment**

- Oxygen ↑ on the carbon/epoxy surface (photo-oxidation)
- C=O (C=O, O=C–OH) ↑ on the carbon/epoxy surface
- Adhesion strength ↑

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**Conclusions**

- Increase in adhesion strength by UV treatment
  - Adhesion strength with respect to UV wavelength
    - UV-B treatment > UV-A treatment
    - UV-B treatment ⇒ 90%↑ in shear strength
    - Failure mode transition
      - Interfacial failure ⇒ adherend failure
  - Excessive UV irradiation caused decrease in adhesion strength due to degradation of adherend

- Interrelation between surface modification by UV and adhesion strength
  - UV-A treatment: little affect surface modification
  - UV-B treatment: oxygen ↑, C=O ↑ on the surface
    - C=O (C=O, O=C–OH) increase on the carbon/epoxy surface
    - Adhesion strength increase