Radiation Curing: Coatings and Composites

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Industrial Electron Beam Markets

- WIRE
- CABLE
- TUBING
- SURFACE CURING
- TIRES
- SHRINK FILM
- OTHER
- SERVICE

>1400 high current EB manufacturing installations
Electron Beam Parameters

Voltage = Electron Penetration
          = Thickness Penetrated

Amperage = Beam Current
           = Exposure Intensity

Kilowatts = Megavolts x Milliamps
            kW = MV x mA
## EB Market Segments Require Different Energies

<table>
<thead>
<tr>
<th>Market Segment</th>
<th>Electron Energy</th>
<th>Typical Penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Curing</td>
<td>80 – 300 keV</td>
<td>0.4 mm</td>
</tr>
<tr>
<td>Shrink Film</td>
<td>300 – 800 keV</td>
<td>2 mm</td>
</tr>
<tr>
<td>Wire &amp; Cable</td>
<td>0.4 – 3 MeV</td>
<td>11 mm</td>
</tr>
<tr>
<td>Sterilization</td>
<td>3 – 10 MeV</td>
<td>38 mm</td>
</tr>
<tr>
<td>Composites</td>
<td>10 MeV</td>
<td>24 mm</td>
</tr>
</tbody>
</table>
80 - 120 keV Development Unit
Low-voltage EB Pilot Line

300 keV self-shielded EB unit for crosslinking film or surface curing
Low-voltage EB Equipment

300 keV self-shielded EB unit for crosslinking film or surface curing
Industrial Electron Beams

5 MeV, 300 kW

10 MeV, 200 kW
X-ray Conversion

Scan Horn

X-Ray Conversion Target

X-Ray Field

Relative Field Intensity
X-ray Depth of Penetration

Dose (kGy) vs. Depth in cm x density, g/cc

- 10 MeV electrons
- 5 MeV X-Rays
- 7.5 MeV X-Rays
Unipolis 10 MeV EB/X-ray Facility
RDI Studies – late 1960s

Walter Brenner and Marsh Cleland
5 July 2005
ADVANTAGES OF RADIATION CURING

Room Temperature Cure
  • Stress-Free Joints.
  • No Thermal Distortion

Saves Energy
  • Eliminates need for Autoclave.

Avoids Air Pollution
  • Solvent is Cured as Part of Resin.
  • No Volatile By-Products.
Surface Tension Tests

Control of water = high contact angle

EB formulation = low contact angle
Surface Tension Tests

Surface Tension, dynes

EB curable coating binders
VARTM with HDPE Platens

Carbon fiber twill sealed in between platens
VARTM with PC/HDPE Platens

Carbon fiber twill sealed in between platens

Wetted carbon fiber
EB/X-ray Cured Sample
Solubility EB/X-ray Cured Samples

~2g resin sample immersed in methylene chloride for ~16 hours

X-ray cured

EB cured

Gel content, %

Dose, kGy
EB Coating Flexibility

Mandrel Bend

0-T Bend
Toughness Testing

Falling tup impact testing:
Eight ply carbon fiber composite matrix with impact additive
Toughness/Impact Testing

Four ply carbon fiber composite and aluminum test panel of comparable thickness: impacted at 13.6 N-m
## Properties Six Ply Carbon Fiber Reinforced Composites

<table>
<thead>
<tr>
<th>X-ray cured in mold at 24 kGy</th>
<th>Initial fracture of matrix</th>
<th>Izod Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>bis-phenol-A diacrylate</td>
<td>6.8 N-m</td>
<td>901 J/m</td>
</tr>
<tr>
<td>matrix system – no impact additive</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bis-phenol-A diacrylate</td>
<td>15.8 N-m</td>
<td>1043 J/m</td>
</tr>
<tr>
<td>matrix system – with impact additive</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Developing Molecular Structures

Molecular weight, $M_n$, and molecular weight between crosslinks, $M_c$, is important.
Developing Molecular Structures

Conventional bis-phenol-A diacrylate

Multiple suppliers, used in radiation curable coatings
Microphase Understanding

Intra-molecular impact additive

Inter-molecular impact additive
Microphase Understanding

Intra-molecular impact additive

Inter-molecular impact additive

SEM to same µm scale
Microphase Understanding

SEM μm scale
amine cured epoxy

AFM nano scale gel
UV cured epoxy diacrylate
Thermal Analysis Resin Systems

<table>
<thead>
<tr>
<th>Resin System</th>
<th>DSC Tg</th>
<th>TMA Tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray cured at 20 kGy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bis-phenol-A diacrylate (Mn = 452)</td>
<td>54°C</td>
<td>66°C</td>
</tr>
<tr>
<td>ethoxylated b-p-A diacrylate (Mn = 572)</td>
<td>----</td>
<td>67°C</td>
</tr>
<tr>
<td>diluted acrylated epoxy-phenolic</td>
<td>92°C</td>
<td>69°C</td>
</tr>
</tbody>
</table>
Dynamic Mechanical Analysis
Dynamic Mechanical Analysis

Used by Charlesby for EB cured styrene-polyesters
Dynamic Mechanical Analysis

Effect of X-ray dose on peak $\tan \delta$ on coating binder/matrix materials
Dynamic Mechanical Analysis

Binder/matrix X-ray cured in mold to 60 kGy
Dynamic Mechanical Analysis

Eight ply carbon fiber X-ray cured in mold to 20 kGy
Pragmatic Tests: TMA

TMA in compression mode
EB XL PE Creep Resistance

Deformation, mm
(TMA constant load at > Tm)

Time, seconds

EVA Tm = 72°C under constant load at 100°C
Heat Deflection Test

Temperature increased at 2°C/minute under constant load
Heat Deflection Test

Six ply composite X-ray cured in mold at 24 kGy

- bis-phenol-A diacrylate matrix system – no impact additive
  - Heat Deflection: >180°C

- bis-phenol-A diacrylate matrix system – with impact additive
  - Heat Deflection: >180°C

Test ended at 180°C = maximum temperature of heating bath
X-ray Curing Studies

Initial X-ray curing carbon fiber composite in the mold
Deep-drawn Fiber Composite
X-ray Curing Composites in the Mold
X-ray Cured Motorcycle Fender
X-ray Cured Sports Car Fender
Conclusions

+ Materials development intended for coatings work can be transformed into use as the matrix system for fiber reinforced composites

+ Tests conducted using low-energy EB can be scaled up to higher energy and X-ray curing

+ X-rays facilitate curing in the mold which can be used for large sized products
Conclusions

+ Some properties developed for coatings are of benefit when binders are used as matrices:
  
  Surface wetting = adhesion
  Flexibility = impact resistance

+ Binders and matrices for EB/X-ray curing should be intentionally designed polymers

+ Fundamental insights into materials should be tempered with pragmatic testing