Introduction to the Basics of UV/EB Chemistry and Formulations

SUNY ESF
Institute for Sustainable Materials and Manufacturing
Dr. Mike J. Idacavage
Esstech, Inc.
September 27, 2012

Agenda

- Introduction to UV/EB Curing
- Basic Formulation strategy
- Oligomers
- Monomers
- Photoinitiators
- Cationic Cure
- Electron Beam
Energy Curable Industrial Coatings

Energy Curable Graphic Arts Applications
What is Energy Curing?

- Using UV energy, visible light, or high energy electrons as opposed to thermal, evaporative, or oxidative (air-dry) cure to form a coating, film or ink

- Types of energy used for energy curing:
  - Ultra Violet (UV): 200 – 400 nm
  - Visible light: typically 380 - 450 nm
  - Electron beam: low energy electrons

While I will try to use the term “energy curable”, please note that the terms “radiation curable or “UV/EB curable” may be used interchangeably.

Why Use Energy Curing?

- Productivity, Productivity, Productivity
  - Seconds to cure vs. minutes or hours

- Lower Overall Cost (per cured part)
  - 100% solids, cure speed, recycling of coating, etc

- Single component formulas
  - Eliminates mixing errors found in 2 component systems

- Regulatory Concerns (VOC emission)
  - Avoid solvent use in most cases

- Smaller equipment footprint
  - Less floor space needed

- Energy costs (esp. now with high oil prices)

- Did I mention Productivity?
Areas of Strength for EC

- Scratch Resistant Coatings (plastic, paper upgrade)
- Over Print Varnishes
- Printing Inks (Litho, Flexo, Screen)
- Wood Coatings
- Electronic & Fiber Optic Coatings
- Photopolymer Plates

EC can generate a high crosslink density network that results in a coating with high gloss and hardness, scratch and stain resistance and fast cure. EC also works best with flat substrates, which are found in all of the above markets.

Areas for Improvement

- Adhesion to some metals, esp. during post-forming
- Adhesion to some plastics
- Tear resistance
- Low gloss in 100 % solid systems
- Low film weight for 100% solids
- Overall cure of 3-D parts

EC coatings can have high shrinkage, which adversely affects adhesion to non-porous substrates. Lack of solvent coupled with a fast cure reduces the formulator’s ability to meet low gloss, low film build requirements. Additional lamps are needed to cure 3D parts since EC is a line of sight cure method.
RADIATION CURING

TYPES OF RADIATION USED

- UV - ultraviolet photons
- EB - low energy electrons

RADIATION CURING CHEMISTRY

- Free Radical
  - Polymerization through double bonds
  - (Meth)Acrylate double bonds most common functionality

- Cationic
  - Polymerization through epoxy groups
  - Cycloaliphatic epoxies most commonly used
RADIATION CURING CHEMISTRY

- **Free Radical Curing - UV**
  - Photoinitiator absorbs UV light and generates free radicals
  - Free radicals react with double bonds causing chain reaction and polymerization

- **Cationic Curing - UV**
  - Photoinitiator absorbs UV light and generates a Lewis acid
  - Acid reacts with epoxy groups resulting in polymerization

- **Free Radical Curing - EB**
  - Electrons open double bonds initiating polymerization - no photoinitiator required

- **Cationic Curing - EB**
  - Electrons decompose photoinitiator to form acid - photoinitiator is required for polymerization
UV CURING

- Acrylated Resin(s)
  basic coating properties
- Monofunctional Monomer(s)
  viscosity reduction, flexibility
- Multifunctional Monomer(s)
  viscosity reduction, crosslinking
- Additives
  performance fine tuning
- Photoinitiator Package
  free radical generation

EB CURING

- Acrylated Resin(s)
  basic coating properties
- Monofunctional Monomer(s)
  viscosity reduction, flexibility
- Multifunctional Monomer(s)
  viscosity reduction, crosslinking
- Additives
  performance fine tuning
Some desirable properties for coatings:

- Adhesion
- Cure speed
- SARC (scratch & abrasion resistant coatings)
- Weatherability
- Flexibility
- Pigmented systems
Formulation of EC Products

All three aspects are interrelated

FORMULATING A UV CURABLE SYSTEM

PHOTOINITIATORS

ADDITIVES

MONOMERS

OLIGOMER
FORMULATING A UV CURABLE SYSTEM

OLIGOMER TYPES

<table>
<thead>
<tr>
<th>(Meth)Acrylated</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxyes</td>
<td>fast curing, hard, solvent resistant, lower cost</td>
</tr>
<tr>
<td>Aliphatic Urethane</td>
<td>flexible, tough, non-yellowing, best weathering properties</td>
</tr>
<tr>
<td>Aromatic Urethane</td>
<td>flexible, tough, lower cost than aliphatic urethanes</td>
</tr>
<tr>
<td>Polyesters</td>
<td>low viscosity, good wetting properties</td>
</tr>
<tr>
<td>Acrylics</td>
<td>good weathering properties, low Tg</td>
</tr>
<tr>
<td>Specialty Resins</td>
<td>adhesion, special applications</td>
</tr>
</tbody>
</table>

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**OLIGOMERS**

**Epoxy Acrylate**

bisphenol A diglycidyl ether diacrylate

**Urethane Acrylate**

aliphatic urethane diacrylate
FORMULATING A UV CURABLE SYSTEM

MONOMERS

Monofunctional Monomer

IBOA
isobornyl acrylate
**MONOMERS**

**Difunctional Monomer**

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{CH}_2\text{=CH-C-O-}(\text{C}_3\text{H}_6\text{O})_3\text{C}-\text{C}=\text{CH}_2 \\
\end{align*}
\]

TRPGDA  
tripropylene glycol diacrylate

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**Trifunctional Monomer**

\[
\begin{align*}
\text{O} \\
\text{CH}_2\text{O-C=CH}=\text{CH}_2 \\
\text{O} \\
\text{CH}_3\text{-CH}_2\text{-C-CH}_2\text{-O-C=CH}=\text{CH}_2 \\
\text{O} \\
\text{CH}_2\text{-O-C=CH}=\text{CH}_2 \\
\end{align*}
\]

TMPTA  
trimethylol propane triacrylate
Like all generalizations, these trends are usually, but not always, true.
ADDITIVES

- Pigments
- Fillers
- Defomers
- Flatting Agents
- Wetting Agents
- Slip Aids

FORMULATING A UV CURABLE SYSTEM

ADDITIVES

PHOTOINITIATORS

MONOMERS

OLIGOMER
Photoinitiators

Terms/Glossary

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{\text{max}}$ (pronounced “lambda max”)</td>
<td>The wavelength at which photoinitiator absorbs the most energy; also known as peak absorbance</td>
</tr>
<tr>
<td>absorbance</td>
<td>The amount of light a material takes in as opposed to reflecting or transmitting it</td>
</tr>
<tr>
<td>cure</td>
<td>The conversion of unreacted material to reacted material; transformation of monomers and oligomers to a polymer network; in practical terms, usually the point at which the wet material reaches a mar free state (or any other property of interest)</td>
</tr>
<tr>
<td>photons</td>
<td>A quantum of light; a packet of light energy</td>
</tr>
<tr>
<td>polymerization</td>
<td>The reaction by which monomers (and oligomers) are converted to high molecular weight materials (polymers)</td>
</tr>
<tr>
<td>radical</td>
<td>AKA free radical, molecule fragment with 1 unpaired electron. Not an ion (has no charge)</td>
</tr>
<tr>
<td>transmission</td>
<td>The amount of light passing through a material; the ratio between the outgoing (I) and the incoming intensity ($I_o$), $%T = (I/I_o) \times 100$</td>
</tr>
</tbody>
</table>
Why Are PI Necessary?

- **PI Characteristics**
  - Absorb UV light or electrons to form active species (radicals or acids)
  - Add to monomer/oligomer to start cure process (polymerization)
  - Different PI absorb UV light at different wavelengths
  - Match PI $\lambda_{\text{max}}$ with UV lamp output
  - Only reacts with UV-Vis energy, not heat
  - Long pot life/shelf life

UV Radical Polymerization

- **Initiation**
  - System is irradiated, reactive species (free radicals) created
- **Propagation**
  - Oligomers and monomers add to the growing polymer chain, creating a high MW network
- **Termination**
  - Two radicals combine to stop the chain reaction
- Photoinitiators can be a factor in initiation and termination
**Initiation**

- **Initiation Process**
  - System is irradiated and the photoinitiator absorbs some of the incoming energy
  - Photoinitiator forms one or more free radicals
  - A free radical then combines with an acrylate to form a new radical that is the active species for the growing polymer
  - UV polymerization is line-of-sight only – shadowed areas very hard to cure

**Propagation**

- **Propagation Process**
  - Referred to as a chain reaction
Termination

- **Termination Process**
  - Two radicals (active species, growing chains, PI fragments) combine and the polymerization stops
  - If PI concentration is too high, the radicals from the PI can contribute to a high termination rate
  - A high termination rate can lead to
    - Greater levels of unreacted material
    - Poor physical properties (e.g. low adhesion, greater marring, poor tensile properties)

Summary

- **Initiation**
  \[ I \xrightarrow{UV \text{ Energy}} 2 \cdot I \text{•} \]
  \[ \cdot I + M \rightarrow IM\text{•} \]

- **Propagation**
  \[ IM\text{•} + M \rightarrow IMM\text{•} \]
  \[ IMM\text{•} + M \rightarrow IMMM\text{•} \]

- **Termination**
  \[ P\sim M\text{•} + \cdot M\sim P \rightarrow P\sim M-M\sim P \]
  \[ P\sim M\text{•} + \cdot I \rightarrow P\sim M-I \]

I = Initiator  M = Monomer (or any acrylate)  P = Polymer chain
Classes of Photoinitiators

- **Photocleavage (unimolecular PI)**
  
a-cleavage PI - Adsorbs light and fragments to form the radicals which initiate polymerization.

- **Photoabstraction (bimolecular PI)**
  
Hydrogen abstraction PI - Adsorbs light and abstracts hydrogen from another molecule (photoactivator) which produces radicals.

Amine synergist (photoactivator) - Donates a hydrogen to the photosensitizer to produce the radicals which initiate polymerization.

Photoinitiator, photosensitizer, and photoactivator are often used as different words for photoinitiators even though they are not the same.

Photoinitiator Mixtures (liquid blends)

- Liquids are easier to handle in a plant (but often $$)

- PI blends offer advantages
  - Absorb over a larger range of wavelengths – better chance of avoiding interference from e.g. pigments and make use of more of the available UV energy
  - Combination of PI for surface and through cure
Photoinitiator Selection

- Absorption characteristics of photoinitiator and formulated system
- Pigmentation
- Spectral output of UV lamps
- Oxygen inhibition
- Weatherability (yellowing)
- Handling (liquid vs. solid)
- Toxicity
- Cost

Matching PI with UV lamp

- Different UV lamps emit energy in different part of the spectrum
- Need to match absorbance of the PI with the output of the lamp for highest efficiency

![Graph showing PI / Lamp Output Match](image)
Oxygen inhibition

- Oxygen can inhibit (slow down) the cure speed of coatings and inks, especially in thin layers

- Solutions:
  - Amine synergists
  - Cure under an inert (N₂) atmosphere

Cationic Cure
CATIONIC CURING MECHANISM

Initiation (Light & Heat)

\[ \text{photoinitiator} \xrightarrow{h_v} \text{initiation} \]

Polymerization (Chain Reaction; Heat)

\[ \text{chain reaction} \rightarrow \text{polymerization} \]
Radical vs. Cationic

**Radical**
- wide variety of raw materials
- inhibited by oxygen
- not inhibited by high humidity
- not inhibited by basic materials
- full cure in seconds
- shrinkage - greater
- adhesion - less
- depth of cure - greater
- cost - less
- UV/EB market share - 92-94%

**Cationic**
- more limited raw materials
- not inhibited by oxygen
- inhibited by high humidity
- inhibited by basic materials
- full cure in hours
- shrinkage - less
- adhesion - greater
- depth of cure - less
- cost - greater
- UV/EB market share - 6-8%

UV Cationic Curing

- **Cycloaliphatic Epoxide(s)**
  - basic coating properties
- **Polyol(s)**
  - crosslinking, flexibility
- **Epoxy/Vinyl Ether Monomer(s)**
  - viscosity reduction
- **Additives**
  - performance fine tuning
- **Photoinitiator Package**
  - cation generation - commonly sulphonium salts
Epoxides

Cycloaliphatic Epoxides

- Major Component of the formulation
- Builds properties of the film
- Other components are modifiers

Electron Beam
ELECTRON BEAM

Ionizing radiation or low energy electrons (e⁻)

- have sufficient energy to break bonds in coating, and generate free radicals
- can penetrate into and through a coating/ink, and through some substrates
- are not affected by pigmentation or transparency of coating/ink or substrate
- generate little to no heat
- dose can be precisely controlled
- enable high throughput

E BEAM PARAMETERS

- **Voltage** = Electron Penetration
  - Equals Thickness Penetrated
  - units are e⁻ volts: MeV, keV
- **Amperage** = Beam Current
  - Equals Exposure Intensity
  - units are amps
- **Dose** = Absorbed Energy
  - Expressed in kGy (kiloGray) or Mrad (mega rad)
High Voltage E BEAM PENETRATION

Low Voltage E BEAM PENETRATION
e⁻ AND hv PENETRATION

LOW VOLTAGE E BEAM
Thank You!

Dr. Mike J. Idacavage  
Director of Business Development  
Esstech Inc.  
Email: mike.idacavage@esstechinc.com  
Phone: 1-610-422-6589