Polyesters Resin
Polyesters (Unsaturated)

• The most common type of resin for composites
• The least expensive composite resin
• The easiest-to-cure composite resin
• Polyesters are made from two types of monomers:
  – Di-acids
  – Glycols
Polyester polymerization

Monomers

Acids A (di-acids)

Glycols G (di-alcohols)

Polyester polymer
Polyester polymerization

- Di-acids have active OH groups on both ends
- Glycols have active H groups on both ends
- One end of the di-acid (the OH group) reacts with one end of the glycol (the H group) to form water (H –OH)
  - The water separates from the polymer and condenses out as a liquid
  - These are condensation polymerization reactions
Polyesters polymerization

1st Step

Ester (new bond)

Many Steps
## Customizing the Polyester – Acids

<table>
<thead>
<tr>
<th>Di-Acids/Anhydrides</th>
<th>Attributes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maleic/Fumaric</td>
<td>Unsaturation (crosslink sites)</td>
</tr>
<tr>
<td>Orthophthalic</td>
<td>Low cost, styrene compatibility</td>
</tr>
<tr>
<td>Isophthalic</td>
<td>Toughness, water/chemical resistance</td>
</tr>
<tr>
<td>Adipic</td>
<td>Flexibility, toughness</td>
</tr>
</tbody>
</table>
Customizing the Polyester–Glycols

<table>
<thead>
<tr>
<th>Glycols</th>
<th>Attributes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>Low cost, rigidity</td>
</tr>
<tr>
<td>Propylene</td>
<td>Excellent styrene compatibility</td>
</tr>
<tr>
<td>Dipropylene</td>
<td>Flexibility, toughness</td>
</tr>
<tr>
<td>Diethylene</td>
<td>Flexibility</td>
</tr>
</tbody>
</table>
## Customizing the Polyester– Solvents

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Attributes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>Cost</td>
</tr>
<tr>
<td>Vinyl toluene</td>
<td>Strength, stiffness</td>
</tr>
<tr>
<td>Acrylic (PMMA)</td>
<td>Low flammability, flexibility</td>
</tr>
</tbody>
</table>
Customizing the Polyester—Adding Other Monomers or Resins

<table>
<thead>
<tr>
<th>Resin</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dicyclopentadiene (DCPD)</td>
<td>Lower cost, improve stiffness</td>
</tr>
<tr>
<td>Styrene butadiene rubber (SBR)</td>
<td>Toughness</td>
</tr>
<tr>
<td>Thermoplastics</td>
<td>Surface quality</td>
</tr>
</tbody>
</table>
Polyesters – specific molecules

The number of repeating units is usually shown by an $n$. 

Isophthalic Polyester

Bisphenol A Fumaric Acid Polyester
Polyesters – crosslinking (curing)

Unsaturated portion

Polyesters must have unsaturated portions to crosslink
Initiators (catalysts)

- Initiators are sometimes called **catalysts**.
- The crosslinking reaction is begun when an **initiator** reacts with the double bond.
- The most common initiators are **peroxides**.
- The peroxides are effective initiators because they split into **free radicals** (that is, they have unshared electrons) which react easily with the double bonds.
- Free radicals have **unshared electrons**.
Polyesters – crosslinking (curing)

Initiator $\rightarrow$ I$\cdot$

$\text{C}=$=$\text{C}$ $\cdots$ $\text{C}=$=$\text{C}$
Polyesters – crosslinking (curing)
Polyesters – crosslinking (curing)

Bond (2 electrons)

Unshared electron
Polyesters – crosslinking (curing)

Free radical (unshared (unbonded) electron)

Free radicals react readily with any Carbon-carbon double bond they encounter.
Polyesters – Reaction Problem

• To react and form a crosslink, the free radical on the polymer needs to encounter (collide with) a double bond on another polymer

• The polymers are long and entangled (highly viscous), thus they don’t move very quickly

• The polymers are bulky and it is hard to get the free radical into the area of the double bond
Polyesters – Reaction Solution

• Dissolve (dilute) the polymer with a solvent so that the polymers can move around freely
  – Ideally, the solvent will react during the crosslinking reaction so that it does not need to be removed from the solid
    • These types of solvents are called “reactive solvents” or “reactive diluents” or “co-reactants”

• Added benefit:
  – The solvent will also reduce the viscosity so that the polymer will wet the fibers more easily
Styrene

- Styrene is the most common solvent for polyesters
- The styrene reacts (is consumed) during the crosslinking reaction because the styrene contains a double bond and reacts with the free radical

\[ \text{C} - \text{C} - \text{C} - \text{C} - \text{C} = \text{C} \]

- The styrene serves as a bridge molecule between the polymer chains (as part of the crosslink)
  - There may be as many as 8 styrene molecules in a bridge
The styrene is a bridge molecule between the polyester polymers. The new free radical is available to react with another styrene.
Crosslinking Reaction

• Called **addition** or **free radical** crosslinking reaction

• Proceeds as a **chain reaction**
  – Once started, it will keep going unless specifically terminated
  – Doesn’t need more initiator
  – Makes its own reactive sites
Inhibitors

• Inhibitors are added, usually by the resin manufacturer, to **slow down** the crosslinking reaction
  – Inhibitors typically **absorb free radicals**
  – Inhibitors **protect the polymer** during storage because sunlight, heat, contaminants, etc. can start the curing reaction
  – Molders must **add sufficient initiator** to overcome the inhibitors and to cause the crosslinking to occur
Promotors (accelerators)

• Added to the polymer to make the initiator work more efficiently or at a lower temperature
  – Each type of peroxide has a temperature at which it will break apart into free radicals
  – These temperatures are usually above room temperature
  – For room temperature curing, a chemical method for breaking apart peroxides is needed

• The most common promotors (accelerators) are cobalt compounds and analines (DMA)

• Never add a promoter directly into an initiator
Additives

• Additives are components (usually minor) that have various functions that are not related to the curing reaction.

• The most common types of additives are:
  – Fillers (to lower cost and/or give stiffness)
  – Pigments
  – Fire retardants
  – Surfactants (to promote surface wetting)
  – UV inhibitors/Anti-oxidants
Factors influencing cure

• Mix ratios
  – Resin, initiator, inhibitor, accelerator, solvent
  – Fillers, pigments, other additives
• Storage time after activation
• Thickness of the part
• Cure time
• Humidity
• Temperature
Thermal effects

• The rate (speed) of chemical reactions increases as the temperature is increased
• Molecular collisions are required
• Heat increases molecular movement
• Highly reactive entities (like free radicals) have successful reactions with almost every collision
Time-Temperature Curve in the sample at constant applied temperature

Temperature $^\circ$F

Temperature $^\circ$C

Time, min
Temperature-Viscosity Curve

- Liquid-Solid Line
- Gel Point
- Region A
- Region B
- Solids
- Liquids

Viscosity

- Thinning due to temperature
- Crosslinking
- Combination (What is seen)
Peroxide content – Temperature and Time Curves

Peak Exotherm, °C

0.5% cobalt naphthenate

% methyl ethyl ketone peroxide (MEKP)

°F
Accelerator Content – Time Curve

Gel Time, Min

At 0.25% MEKP

At 0.50% MEKP

% Cobalt Naphthenate
Polyesters
Epoxies
Epoxies

- **Second** most widely used family of thermosets (after polyesters)
- Large portion of uses are **non-reinforced** (adhesives, paints, etc.)
- **Circuit boards** are the largest reinforced application (low conductivity, low volatiles)
- **Advanced composites** use epoxies because of
  - Thermal stability
  - Adhesion
  - Mechanical properties
Epoxy Structure

- Epoxy ring
- Polymer portion
- Number of repeat units
Epoxy – specific molecules

a) **Diglycidyl Ether of Bisphenol A (DGEBPA)**

b) **Tetraglycidylmethylenedianiline (TGMDA)**

c) **Epoxidized phenolic resin (Epoxy Novalac)**
Epoxy – specialty molecules

Toughened Epoxy Resin

High Temperature Epoxy Resins
Curing Epoxies

• Epoxies use hardeners instead of initiators for curing
• Hardeners can be almost any molecule that will react with (open) the epoxy ring
Epoxy Crosslink Mechanism

The other end can also react.

Cured Polymer
Curing

Hardener molecules have two reactive ends, so they can each react with two epoxy molecules.
# Effects of various hardeners

<table>
<thead>
<tr>
<th>Hardeners</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic amines</td>
<td>Convenience, low cost, room temp cure, low viscosity</td>
<td>Skin irritant, critical mix ratios, blushes</td>
</tr>
<tr>
<td>Aromatic amines</td>
<td>Moderate heat resistance, chemical resistance</td>
<td>Solids at room temp, long and elevated cures</td>
</tr>
<tr>
<td>Polyamides</td>
<td>Room temp cure, flexibility, toughness, low toxicity</td>
<td>High cost, high viscosity, low HDT</td>
</tr>
<tr>
<td>Amidoamines</td>
<td>Toughness</td>
<td>Poor HDT</td>
</tr>
<tr>
<td>Dicyandiamide</td>
<td>Good HDT, good electrical</td>
<td>Long, elevated cures</td>
</tr>
<tr>
<td>Anhydrides</td>
<td>Heat and chem resistance</td>
<td>Long, elevated cures</td>
</tr>
<tr>
<td>Polysulfide</td>
<td>Moisture insensitive, quick set</td>
<td>Odor, poor HDT</td>
</tr>
<tr>
<td>Catalytic</td>
<td>Long pot life, high HDT</td>
<td>Long, elevated cures, poor moisture</td>
</tr>
<tr>
<td>Melamine/form.</td>
<td>Hardness, flexibility</td>
<td>Elevated temp cure</td>
</tr>
<tr>
<td>Urea/form.</td>
<td>Adhesion, stability, color</td>
<td>Elevated temp cure</td>
</tr>
<tr>
<td>Phenol/form.</td>
<td>HDT, chem resistance, hardness</td>
<td>Solid, weatherability</td>
</tr>
</tbody>
</table>

MKR 1153
## Epoxy and Polyester Comparison

<table>
<thead>
<tr>
<th>Comparisons</th>
<th>Polyester</th>
<th>Epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active site</td>
<td>C=C</td>
<td>C=O</td>
</tr>
<tr>
<td>Crosslinking reaction</td>
<td>Addition/free radical</td>
<td>Ring opening</td>
</tr>
<tr>
<td>Crosslinking agent</td>
<td>Initiator (peroxide)</td>
<td>Hardener</td>
</tr>
<tr>
<td>Amount of x-link agent</td>
<td>1-2% of resin</td>
<td>1:1 with resin</td>
</tr>
<tr>
<td>Solvent/viscosity</td>
<td>Styrene (active)/low</td>
<td>Infrequent/high</td>
</tr>
<tr>
<td>Volatiles</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Inhibitors, accelerators</td>
<td>Frequent</td>
<td>Infrequent</td>
</tr>
<tr>
<td>Reactant toxicity</td>
<td>Low</td>
<td>Moderate</td>
</tr>
<tr>
<td>Cure conditions</td>
<td>Room temp or heated</td>
<td>Heated (some room)</td>
</tr>
<tr>
<td>Shrinkage</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Post cure</td>
<td>Rare</td>
<td>Common</td>
</tr>
</tbody>
</table>

MKR 1153
## Polyester and Epoxy – Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Polyester</th>
<th>Epoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adhesion</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Shear strength</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Fatigue resistance</td>
<td>Moderate</td>
<td>Excellent</td>
</tr>
<tr>
<td>Strength/stiffness</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Creep resistance</td>
<td>Moderate</td>
<td>Moderate to good</td>
</tr>
<tr>
<td>Toughness</td>
<td>Poor</td>
<td>Poor to good</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Moderate</td>
<td>Good</td>
</tr>
<tr>
<td>Electrical resistance</td>
<td>Moderate</td>
<td>Excellent</td>
</tr>
<tr>
<td>Water absorption resist</td>
<td>Poor to moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Solvent resistance</td>
<td>Poor to moderate</td>
<td>Good</td>
</tr>
<tr>
<td>UV resistance</td>
<td>Poor to moderate</td>
<td>Poor to moderate</td>
</tr>
<tr>
<td>Flammability resistance</td>
<td>Poor to moderate</td>
<td>Poor to moderate</td>
</tr>
<tr>
<td>Smoke</td>
<td>Moderately dense</td>
<td>Moderately dense</td>
</tr>
<tr>
<td>Cost</td>
<td>Low</td>
<td>Moderate</td>
</tr>
</tbody>
</table>
Epoxy
Vinyl Ester Resins
Vinyl Esters

- Epoxy resins that have been modified so that they can be cured like a polyester
  - The modification is usually a reaction with an acrylic (acrylic modified epoxy)
  - The modification must substitute a carbon-carbon double bond for the epoxy ring
Vinyl Ester Structure

Unsaturated end group

Unsaturated end group

Unsaturated end group

Unsaturated end group
Vinyl esters – specific molecules

Methyl Acrylic Acid

Epoxy

Vinyl Ester

Epoxy

Vinyl Ester
Specialty Vinyl Esters

Epoxy Novolac Vinyl Ester Resin

Bisphenol-A Epichlorohydrin-based vinyl ester
Vinyl esters – Properties

• Almost all properties of vinyl esters (and cost) are intermediate between polyesters and epoxies
• Some of the most important properties include:
  – Water and chemical resistance
  – Electrical stability
  – Thermal stability
  – Toughness
  – Low volatiles during manufacture
  – Low shrinkage
Vinyl Esters
Epoxy adhesive