Overview of Resins used in FRP Equipment

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Outline

- Resin fundamentals
- Importance of veil
- Requirements for Successful applications
- Testing for corrosion resistance
- Summary and conclusions
Successful Application Details

• Resin Selection
• Design/Engineering
• Writing Specifications
• Fabrication
• Inspection
Resin Selection Criteria

- Chemicals
- Concentrations (Max./Min.)
- Temperatures (Operating/Max./Min.)
- Upsets
- Flame Resistance
- Abrasion
- Insulation
- Manufacturing Process
Resins / Polymers

Thermoset

Egg

Thermoplastic

Candle
Types of Resins used in Corrosion Applications

- Thermoset Resins
  - Unsaturated Isophthalic Polyester resins
  - Chlorendic Polyester resins
  - Bisphenol A Fumarate
  - Epoxy vinyl ester resins
  - Epoxy Resins
  - Furfural Alcohol Resin
History Of Corrosion Resistant Resins Development Timeline

Bisphenol-A Fumarate Polyester

1950

Chlorendic Polyester

1960

Dual Laminates

Vinyl Ester

1970

Novolac V.E.

1980

Hi-Performance V.E.

1990

Improved HDT EVERs

2000

Improved Toughness EVERs

“50 Years of Proven Performance”
Generic Thermoset Resins

- Unsaturated Isophthalic Polyester resins
- Chlorendic Polyester resins
- Bisphenol A Fumarate
- Epoxy vinyl ester resins
- Epoxy Resins
- Furfural Alcohol Resin

- General Purpose
- Strong acids and oxidizers
- Acids and bases
- Acids, bases, tough
- High pressure piping
- Organic solvents and caustic
Polyester Resins

Polyester resins are a reaction of a difunctional acid and a difunctional alcohol (glycol). The reaction forms an ester with water given off as a by-product.
Basic Polyester Chemistry

Polyester Components

Cross linking acid

Glycol

Functional Acid

Functional Acids
- Orthophthalic acid
- Isophthalic acid
- Terephthalic acid
- DCPD
- Adipic acid

Glycols
- Propylene glycol (PG)
- Dipropylene glycol (DPG)
- Ethylene glycol (EG)
- Diethylene glycol (DEG)
- Neopentyl glycol (NPG)
Crosslinks with styrene

CH\equiv\text{CH}_2·-

liquid styrene monomer

A) SOLVENT

B) COREACTANT
Common POLYESTER Resins

isophthalic acid + propylene glycol + fumaric acid

UNSATURATED THERMOPLASTIC POLYESTER
Typical Applications:
- Aqueous environments
- Gasoline tanks
- Acids

Typical Applications:
- Aqueous environments
- Filament winding
- Impact resistance
- Thermal shock resistance
Chlorendic Anhydride Resins

- Exceptional corrosion properties in oxidizing acidic environments
- Inherently fire resistant
- Limited toughness
Typical Applications

- Premium Corrosion Service
- Unmatched Corrosion Properties in Oxidizing Acidic Environments
Bisphenol A Fumarate Polyester Resins

• Date back to the 1950’s
• Originally used in pulp bleaching and chlorine dioxide storage
• Later used in chlor-alkali production
• Superior to earlier polyesters in both oxidizing and caustic environments
Pulp & Paper
EPOXY RESIN

bisphenol A + epichlorohydrin
Epoxy Resins

- Epoxy resin properties dependent on hardener used to cure resin
- Typical hardeners
  - Aromatic amines
  - Aliphatic amines
  - Anhydrides
- Ashland does not make Epoxy resins
- Used in high pressure pipe applications
Epoxy Vinyl Ester Resins

Chemical Structure
Features and Benefits
Novolac, Brominated, and Elastomer Modified Epoxy Vinyl Ester Resins
What is an Epoxy Vinyl Ester Resin?

• Epoxy methacrylate

• A reaction product of epoxy resin and methacrylic acid with a reactive diluent

• Styrene acts as a reactive diluent

• Cures at room and elevated temperature

• Compatible with all fabricating processes
**Epoxy Vinyl Ester Resins**

Formation of Epoxy Vinyl Ester Resins - General Reaction Scheme

Bisphenol-A Epoxy Resin + Methacrylic Acid → Polymerisation → Catalyst DT → Bisphenol-A Epoxy Vinyl Ester Resin
Features of an Epoxy Vinyl Ester Resin

• Molecular Structure

1. Terminal Carbon-Carbon double bonds promote reactivity & complete cure
Features of an Epoxy Vinyl Ester Resin

• Molecular Structure

2. Ester groups are subject to chemical attack or hydrolysis. An epoxy vinyl ester only has two ester groups, a polyester has many
Features of an Epoxy Vinyl Ester Resin

• Molecular Structure

3. Ester groups that do occur are protected from hydrolysis and chemical attack by Methyl-shielding
Features of an Epoxy Vinyl Ester Resin

- **Molecular Structure**

  4. Multiple secondary Hydroxyl groups along the molecule chain promote wetting and adhesion to glass fibers
Features of an Epoxy Vinyl Ester Resin

• Molecular Structure

5. Less reactive (stable) ether bonds hold the chain together
Features of an Epoxy Vinyl Ester Resin

- Molecular Structure

6. Tough Epoxy Backbone
Features of an Epoxy Vinyl Ester Resin

• Summary Structure/Property Relations

Only two Ester groups per chain

Epoxy Backbone \[ \Rightarrow \] Toughness
Sec. OH-Groups \[ \Rightarrow \] Adhesion & Wetting
Methyl-group shielding \[ \Rightarrow \] Chem. Resistance
Terminal C=C-Bonds \[ \Rightarrow \] Reactivity
Bisphenol A Epoxy Vinyl Ester Resins

• Benefits
  – Broad corrosion resistance superior to high alloy metals
    • Acids
    • Bases
    • Bleach
    • Salts
    • Solvents
  – Toughness
  – FDA Compliance
Epoxy Vinyl Ester Resins

- Tough Resin
- Typical Applications:
  - Aqueous
  - Mild organic solvents
  - Acids
  - Bases
Novolac Epoxy Vinyl Ester Resin

High Crosslink Density = improved heat and solvent resistance
NOVOLAC EPOXY VINYL ESTER RESINS

Epoxy Novolac Resin Based Benefits

• Excellent Resistance to Oxidizing Acids
• Superior High-Temperature Stability
• Superior Solvent Resistance
Applications
Brominated Epoxy Vinyl Ester Resin

Bromine on backbone = chemical stability and fire retardancy
Brominated Epoxy-Based

Benefits

• Fire Retardancy (By Bromination, Not Additives)

• Broad Chemical Resistance

• Excellent Toughness
POLYESTERS

VINYL ESTERS
CURING

\[ \text{MEKP} + \text{PROMOTER} \rightarrow \text{R}_1 - \text{O} - \text{PROMOTER} \]

\[ \text{cobalt napthenate} \]

\[ \text{LEVEL OF CATALYST} \]
\[ \text{LEVEL OF PROMOTER} \]
\[ \text{ANILINE} \]
Furan Resin

FIG. 2
Furan Resin

FIG. 3

crosslink reaction

Furfuraldehyde
Furan resin

- Used for its Solvent Resistance
- To 300° F.
- Fabrication Critical

- Typical Applications
  - Excellent solvent resistance
  - Acidic and basic resistance
  - Reduced oxidizing resistance
## Generalized Chemical Resistance

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Typical Laminate Construction For Corrosion Resistant FRP

Primary corrosion barrier – minimum of 100 mils – 2.6 mm

Chemical environment

Optional Nexus veil layer

Alternate layers of mat/ woven roving or filament winding

Resin/wax Topcoat With U.V. protection

- C-veil or Nexus polyester veil - 10 mils - 0.25mm - 90% resin
- Chopped strand mat - 1.5 oz/ft2 - 450g/m2 - 70 - 75% resin
- Woven roving - 24 oz/yd2 - 800 g/m2 - 50 - 60% resin
Or filament winding
Evaluation Of Corrosion Resistance

• ASTM C581 Standard Construction
• Corrosion Barrier is Tested
• Evaluation of Test Coupons
  – Barcol Hardness
  – Flexural Strength
  – Flexural Modulus
  – Appearance
  – Weight and Thickness
ASTM C-581 Test Coupon
Standard Construction

10 mil glass veil

3 plies 1.5 oz. glass mat

*Not to Scale*
ASTM C-581 Test Procedure
ASTM C-581 Samples – After Testing
ASTM C-581 Laminate Strength Retentions Profiles

Months Exposure

% Strength Retention

A
B
C
D, 1/4” thick
D, 1/8” thick
E
F

Pass
Fail

0 1 3 6 12

0 50 100
C-glass, ECR glass or Boron free E glass = Chemically resistant glass.

Suitable for most environments except those attacking glass such as: hydrofluoric acid, sodium hydroxide and other chemicals.
Synthetic Surfacing Veils

- Polyester veil.
- Polyacrylonitrile (PAN) veil.
- Developed for hydrofluoric acid and sodium hydroxide applications.
- Apertured version best for visual and corrosion properties.
Carbon Veil

- Used for certain chemicals, instead of C-veil, such as sodium hydroxide and hydrochloric acid.
- Used for electrical conductivity, such as for FRP electrostatic precipitators and FRP fans, with grounding.
- Can be substituted by graphite used with the resin in the corrosion barrier.
- Also used as target for spark testing behind thermoplastics in a dual laminate construction.
Veils
E = Electrical grade glass.
ECR or boron-free E Glass = Electrical corrosion resistant glass.
ECR glass is less soluble in most acids than E-glass. It improves acid resistance at all acid concentrations and dramatically reduces strain corrosion at all acid concentrations.
Type: E-glass = OK. ECR-glass or boron-free = better.

Applied in a corrosion barrier as two or three 1.5 oz/ft² - 450 g/m² layers with a 75% resin content.

Standard corrosion barrier: V/M/M - 100 mils – 2.6 mm.

Four or more plys may be specified depending on the chemical nature of the environment:
  - 200 mils - 5.2 mm.
  - This could go to 500 mils - 13 mm (for hot wet chlorine service).

Applied by hand lay up with the resin and rolled up for air releasing.

Used in alternate layers with woven roving in the laminate structure.
FRP has been used for over 50 years in corrosion applications

Resin selection critical

Corrosion barrier construction critical

Reinforcements used will depend on required structural properties
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