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Resins for FRP Composites

The resins used for manufacturing FRP composites are a broad class defined as “thermoset” resins. Unlike a “thermoplastic” resin (such as polyethylene, PVC, polypropylene) a thermoset resin once it is “cured” takes its final as formed shape. A thermoplastic resin will “melt” with high heat, returning to its original shape.

A thermoset resin used as the matrix in a composite laminate starts its life as a liquid. It is then reacted with a curing agent to cross link into its final polymer, typically after adding the liquid resin to the reinforcement used in the laminate.

The types of thermoset resins used in manufacturing composites include:

1. **Epoxies:** An epoxy resin is manufactured from a petroleum base, and for composites is typically 100% solids (i.e. having no volatile components). The epoxy resins are used for their great strength, high performance, good temperature resistance, and good overall corrosion resistance (depending upon the service environment). The epoxies are reacted (cross linked) by using a wide range of curing agents or hardeners; including amines, anhydrides; and specialty reactants.

The final properties of a reacted epoxy composite laminate depends entirely upon the specific curing agent or hardener that is used to cross link the polymer. The same epoxy resin can be reacted to be as hard or brittle as a pane of glass, or as tough and having the elongation of a sheet of rubber; depending upon what curing agent is used to react the polymer. Included in this broad category of epoxies are:

A. **Standard Epoxies:** Based on bisphenol A or bisphenol F “backbones”: This standard grade of epoxy is used extensively for military, commercial aviation, aerospace, and other applications requiring high performance and good structural strengths.

B. **Novolac Epoxies:** This grade of epoxy has higher temperature properties. But, in curing it becomes more highly cross linked and cured laminate tends to be more brittle. Applications can include automotive, military and aerospace, and other applications when higher temperatures are required.

C. **Phenol Novolac Epoxies:** This type of epoxy resin is more highly cross linked. As a result, it has higher temperature capabilities, to over 600 deg. F,. It also has unique chemical resistance, including chemicals such as 98% sulfuric acid. The phenol novolac epoxies are often used in applications requiring superior corrosion resistance. They are “brittle”, though, unless they are toughened with other additives or modifiers.

2. Polyesters: There are both thermoplastic and thermoset polyester polymers. For our reinforced composite work, we work with the thermoset versions only. The polyesters are one of the earliest thermoset resins - with commercial versions being introduced after World War II. The major classes of polyester resins used in corrosion resistant equipment include:

A. **General Purpose Polyester.** This is a polyester resin that has medium corrosion resistance. It is typically used for applications such as boats, bathtubs and shower stalls, kitchen counter tops, and some automotive parts. Its major advantage is its relatively low cost, ease to work with, and it is available in literally hundreds of formulations and versions. .

B. **Polyesters - Isophthalic and Teraphthalic.** These are polyester resins that are made with isophthalic or teraphthalic acids - and provide superior strength properties and good corrosion resistance. They come in versions that are relatively rigid when cured into laminate; along with versions that have increased toughness and impact strength. Typical uses for this class of polyesters include air handling ducts, cooling water piping, storage tanks and sewage piping.

C. **Polyesters - Bisphenol Fumarate**: This class is the most corrosion resistant of all the polyesters. The resin is highly cross-linked which provides the enhanced corrosion resistance. It is a very brittle resin. To be successfully shipped, handled, and installed often requires the use of a resin flexibilizer. This flexibilizer does reduce the corrosion resistance and maximum operating temperatures. Bisphenol fumarate polyesters are available in both fire retardant and non-fire retardant versions.

3. **Epoxy Vinylesters**: This group of resins has rapidly become the “work horse” of the corrosion and allied industries. The vinyl ester resin is made by modifying epoxy resins with acrylic “linkages” in the polymer backbone. The resulting hybrid resin has generally very good corrosion resistance, superior toughness, and is relatively easy to successfully fabricate into composite components.

Unlike the standard epoxy resins, which require special hardeners and typically, to gain the optimum properties, a heat post cure, the acrylic modified vinylester epoxy resins can be cross linked using peroxide catalysts at room temperatures.

A. **Epoxy Vinylesters** - Standard Premium Grade: Suitable for a wide variety in chemical service enviroments at temperatures up to 220 deg. F. This grade of epoxy vinylester finds use as corrosion resistant tanks, duct, piping, and specialty products - where its unique properties can provide significant benefits to the end user. The standard premium grade epoxy vinylester are available in both fire retardant and non-fire retardant versions.

B. **Epoxy Vinylester - High Performance, High Temperature:** These resins are manufactured using acrylic modified Novolac epoxy resins. They provide the end user enhanced chemical resistance for many service environments; including some of the solvents. The Novolac epoxy vinylester resins offer superior high temperature physical properties - as well as higher service chemical service environments for temperatures up to 350 deg. F.

This Novolac grade of epoxy vinylester is used in a wide range of high temperature chemical service environments; including tanks, pipes, ducts, stacks, etc. Because of its novolac base, it does however have less toughness (i.e. a lower tensile elongation) and this is a more brittle laminate than the standard premium grade epoxy vinylester. The Novolac epoxy vinylester is also available in both fire retardant and non-fire retardant versions.

C. **Epoxy Vinylesters - Elastomeric Modified:** This grade of epoxy vinylester resins is manufactured with a elastomeric or rubber additive that is included at the time the base resin is made. The amount of rubber or elastomer added can vary.

By including the elastomeric modifier into the already tough vinylester epoxy resins, you gain superior toughness, improved adhesion to other laminates and substrates (such as metal and concrete), and improved impact resistance. The elastomeric modified epoxy vinylester resin also offers improved abrasion resistance - almost doubling the wear resistance over a standard epoxy vinylester.

Typically uses for the elastomeric modified epoxy vinylester include: Abrasion liners for high wear slurry piping; fire and safety helmets, kayak, heavy duty flanges, automotive parts, and coatings and linings. The addition of the elastomer does reduce corrosion resistance in certain chemical environments. And, it also reduces the maximum operating temperatures. The elastomeric modified epoxy vinylester resins are often also used in blends of the other epoxy vinyl esters, to increase toughness and to prevent cracking and crazing of the laminate.

4. Urethanes: The urethane thermoset polymers are relatively new for composites. Reichhold Chemical has one urethane modified resin that competes with the epoxy vinylesters for pipe and other composite applications that require excellent toughness, with still provides very good corrosion resistance.

The urethanes may find application also for abrasion resistant slurry piping and baffles in slurry mixing tanks.

100% urethane thermoset resins have been used for high impact piping systems, blades for large wind powered generators, and automotive applications. The all (100%) urethane resins are typically reacted with an isoeynate to yield a composite that is very tough, having a high elongation (similar to that of rubber). For the urethane there are limitations on temperature. However, the primary use of the urethane resins has been in those applications where high impact and toughness are overriding.

One of the processing problems of the thermoset urethane is a very short pot life. However, this can be solved.

5. Furans: This unique thermoset resin, because of its many processing problems, has not gained the usage that it merits. The base furfural from which furan is made, are from corn cobs and oat hulls. Thus, it is a composite polymer that is truly derived from renewables. And, in this case, agricultural waste products.

When used as the resin matrix for duct, tanks and pipe, furan resins provide excellent chemical service for a wide range of acids and solvents. Furan is the only composite laminate that will handle nasty solvents - such as methylene chloride, toluene, monochlor benzene, tetrahydrafuran, etc. The pharmaceutical, semi-conductor, and chemical industries are major users of furan composites

Properly formulated cured and furan resins will also provide outstanding fire retardarncy, including low flame spread and low smoke generation. In Factory Mutual testing, the furan laminates have proven that they can handle temperatures up to 1900 deg. F; and never catch on fire, burning or collapsing.

So why, with all of these amazing properties, are not furan resins used more for corrosion applications? Furan resins are extremely difficult to use in fabricating composite laminates with. The cross linking (curing) of the furan resins is accomplished by reacting with acids. The reaction is a condensation reaction, which creates one molecule of water in the polymer chain where each cross linking occurs. And, for maximum corrosion resistance furans need to be post cured. The initial and post curing has to be kept below the boiling point of water - so as not to cause destruction of the laminate.

Very careful control of the curing process of furan resins must be observed to prevent the exotherm from exceeding 212 degrees F. Otherwise, the water being generated will become steam - causing porosity, blisters and delaminations in the laminate!

In addition, the standard acid catalysts for furan resins provide a 7-10 minute pot life - which is not long enough to allow easy lamination of large parts or long lengths of pipe. The typical furan resin also has a very low tensile elongation, and thus is brittle and must be handled “gently” in manufacturing, shipping, handling, and installation.

Over the years, many fabricators have tried using the furan resins because of their unique and multiple benefits to the end user. But, with all of these processing problems, many have given up.

Some fabricators have tried to get around the processing problems by using a very thin inner corrosion barrier of furan, backed by a resin system that is easier to fabricate with. The results of this “dual laminate” have been disastrous. The more corrosive media will penetrate that thin furan barrier, destroying the less chemical resistant resin used as the backing or structural laminate.

Fortunately, there are fabricators who have learned how to control the exotherm during the initial and post curing. They have also learned how to control the pot life, extending it to all fabrication of longer or larger parts. The more knowledgeable fabricators have learned how to increase the toughness and how to control brittleness.

6. Phenolics: Phenolics are one of the oldest thermoset resins. Its roots go back to the late 1890's when it was first introduced for making billiard balls. Because of its excellent high temperature properties, it also was the standard for many years for the resin matrix used in making automotive brake pads.

Depending upon the manufacturer (there are several) phenolic thermoset resins are made from resorcinol and/or formaldehyde. There are also both base and acid cured versions. Most of the corrosion resistant phenolic are acid cured. Just as with the furans, with the acid cured resins, the cross linking is a condensation reaction which gives off water. This requires careful attention and detail to the curing and post curing sequences.

The phenolics have outstanding fire retardarncy; low smoke generation; and perhaps most importantly for high occupancy situations, low smoke toxicity. The phenolics are the only resins that meet the New York Fire Marshall’s requirements for low smoke toxicity.

Typical applications for phenolic composites include: Ductwork in high occupancy buildings, ducting for the semi-conductor industry, seats on subways, the wall panels for the "chunnel" between England and France, and personnel protective fire pods on offshore oil platforms.