Different FRP Resin Chemistries for Different Chemical Environments

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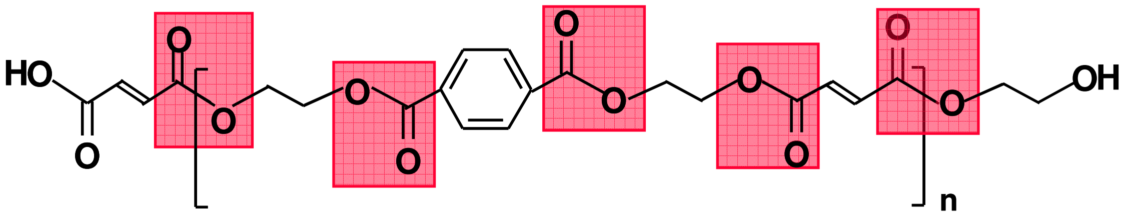
ABSTRACT

The corrosion challenges posed by different chemical environments mandate the use of a variety of resins for the fabrication of durable fiberglass-reinforced plastic (FRP) equipment. Different resin chemistries can provide widely different performance in a given chemical environment. To a great extent, the chemical resistance of FRP depends largely upon the resin composition used to encapsulate glass fiber reinforcements and lock them into a desired shape. The purpose of this paper is to provide an overview and history of FRP resin chemistries that can be used in various chemical environments and how these chemistries can affect FRP corrosion performance.

INTRODUCTION

Since the introduction of FRP into chemical processes more than half a century ago, improvements in resin chemistry and fabrication techniques have made FRP highly competitive with corrosion-resistant metal alloys such as stainless steel and high nickel alloy. Many factors go into making FRP projects successful, but success always begins with choosing the appropriate resin for the chemical environment in which the equipment will be used. In corrosion applications, resins encapsulate glass fiber reinforcements to provide them with protection from chemical attack. In order for a resin to be suitable for a given chemical environment, it must be resistant to the chemical at the various concentrations and operating temperatures to which it will be subjected. Following a brief description of early FRP use, this paper will look at the chemistry of corrosion-resistant FRP resins starting in the 1950s, and then trace their evolution into the 21^{st} Century.

Following World War II, FRP first gained prominence as a construction material for radar domes and marine vessels. In fact, the first large-scale use of FRP was in the pleasure boat industry. Fiberglass vessels were lightweight, less expensive to construct than wooden vessels, and possessed excellent corrosion resistance to seawater. However, the polyester resins used for building boats, (Figure 1), were not suitable for most chemical-resistant applications. These resins have multiple ester groups along the backbone - from which the name polyester was derived. Ester groups are often susceptible to chemical attack. As a result these resins were not considered to be suitable for more aggressive environments such as chlorine, bleach, caustic, and strong acids.



n = 3 to 6

Figure 1. Typical Polyester Resin Backbone with Multiple Ester Groups

By the late 1950s, the use of FRP equipment had expanded to chemical processing environments as well as pulp bleaching plants. In these applications FRP materials replaced more expensive and often less durable metal alloys, rubber lined steel, and wood. In the late 1960s, epoxy vinyl ester resins were introduced, significantly improving FRP service life via further enhanced chemical resistance and toughness. The use of FRP in aggressive chemical environments was further improved with the introduction of novolac epoxy vinyl ester resins in the early 1970s with greater resistance to both heat and organic solvents. Corrosion-resistant resin technology continues to evolve and improve as it adapts to the ever-growing demands of the corrosion market.

EARLY CHEMICAL RESISTANT RESIN CHEMISTRY

In the 1950s, chemically resistant FRP resins were found primarily in the pulp and paper and chemical process industries. The first polymers used to fabricate corrosion-resistant composites were polyester resins synthesized from Bisphenol A and fumaric acid. In the pulp and paper industry, Bisphenol fumarate–based FRP replaced the wood and tile materials which were currently employed in chlorine dioxide storage and pulp bleaching. The chemical structure for this type of polyester resin is shown in Figure 2. FRP made from these resins has superior resistance to both oxidizing and caustic environments as compared to the earlier polyester resins used to make boats. Consequently, these resins have also been used extensively in the chemical process industry, (e.g. chlor alkali production).

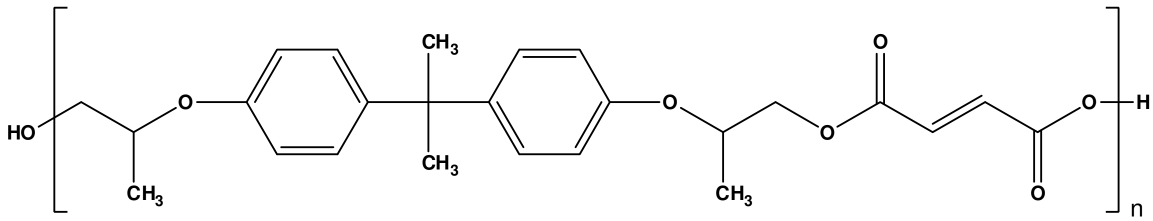


Figure 2. Bisphenol A Fumarate Polyester Resin Polymer Structure

The next chemical-resistant resin to be introduced was Chlorendic acid polyester resin (shown in Figure 3). FRP made with Chlorendic polyesters is particularly resistant to wet chlorine gas as well as oxidizing acids such as nitric acid, sulfuric acid, and chromic acid. It is still widely used by chlorine manufacturers today. However, it and most polyester resins are not suitable for caustic environments.

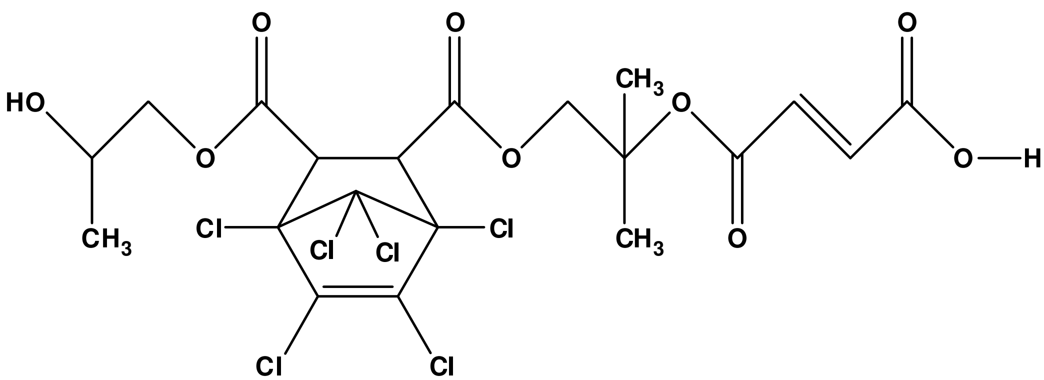


Figure 3. Chlorendic Polyester Resin Polymer Structure

Both Chlorendic and Bisphenol fumarate resins provided a big improvement in corrosion performance over earlier polyester resins. Unfortunately, FRP made from these resins tended to crack, not only during use, but also during fabrication and transport. New technology was needed to make tougher, crack-resistant FRP without reducing its chemical resistance.

EPOXY VINYL ESTER RESINS

In the late 1960s, Bispenol A epoxy vinyl ester resins answered this challenge. FRP made with Bisphenol A “vinyl esters” was much tougher than earlier polyester technology. These tougher composites were also much more resistant to mechanical and thermal stress. As a result, FRP made from Bisphenol A “vinyl esters” could be used in a wide variety of chemical environments. Moreover, they possessed an increased level of chemical resistance equal to or better than more expensive high nickel alloys such as C-276 and superior to 2205 duplex (ferritic / austenitic) stainless steel (see Table1).

Table1. The Chemical Resistance of FRP Made From Epoxy Vinyl Ester Resin Compared to 2205 Stainless Steel and Alloy C-276

Materials	**Sulfuric Acid**	**Hydrochloric Acid**	**Acid Chloride Salts**
FRP Made with Epoxy Vinyl Ester Resin	**100ºC to 30%**	**80ºC to 15%**	**100ºC all concentrations**
2205 Stainless Steel	**30ºC to 30%**	**60ºC to 1%**	**65ºC to 2000 ppm @ low pH**
Alloy C-276	**100ºC to 30%**	**80ºC to 15%**	**65º to 50,000 ppm@ low pH**

Figure 4 highlights the chemical structure of Bisphenol A "vinyl ester" resins. Note that these resins have only two ester groups per molecule (highlighted below). This is significant in that ester groups can be susceptible to chemical attack. Fewer ester groups generally translates to better chemical resistance. The Bisphenol A epoxy group, shown in the brackets, imparts toughness to the resin making it more resistant to thermal and mechanical stress. These resins also have multiple ether linkages which further add to their chemical resistance. Finally, the resin backbone has multiple hydroxyl groups (-OH) that function to enhance adhesion to fibers and other composite materials (through hydrogen bonding). FRP equipment based upon Bisphenol A epoxy "vinyl ester" resins has been so successful in chemical service that they have largely displaced Bisphenol fumarate resins and have become the industry standard in the corrosion-resistant resin market.

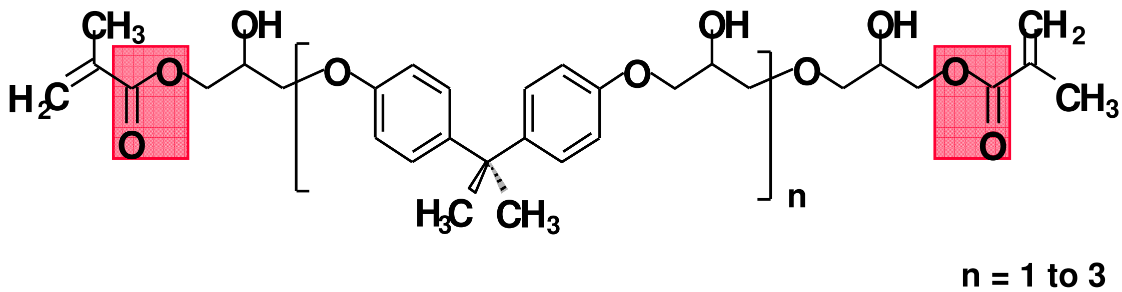


Figure 4. Bisphenol A Epoxy “Vinyl Ester” Resin Polymer Structure

Epoxy vinyl ester resins were again improved in the early 1970s with the incorporation of Novolac chemistry. Novolac functionality enables FRP equipment to withstand higher service temperatures. Novolac epoxy vinyl ester resins are also characterized by enhanced resistance to organic solvents. Reviewing Figure 5, one can see that the Novolac epoxy vinyl ester has three vinyl groups per molecule. When these groups polymerize, they form a highly cross-linked polymer. Cross-linking makes it more difficult for solvents to penetrate the polymer structure and also increases the polymer's glass transition temperature thus providing improved heat resistance.

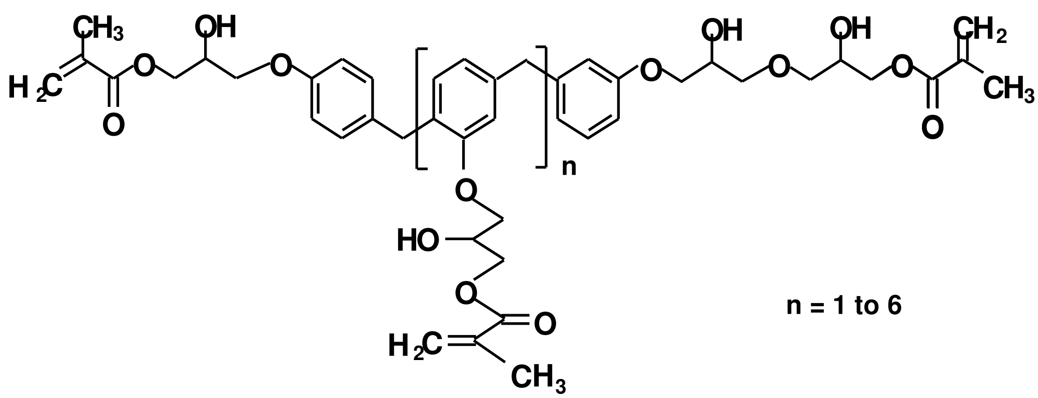
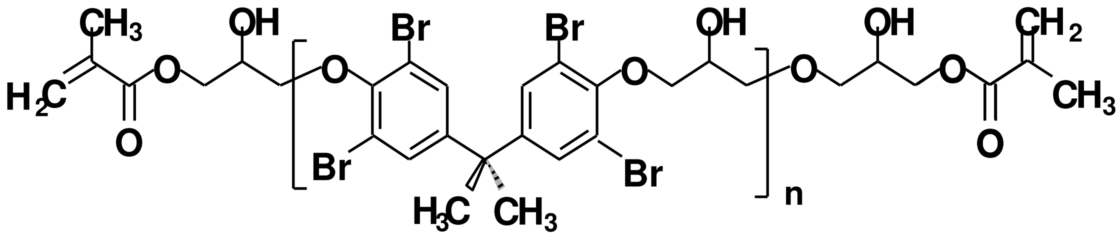


Figure 5. Epoxy Novolac Vinyl Ester Resin Structure

The next major development was the introduction of brominated epoxy vinyl ester resins. These resins delivered fire retardance in addition to corrosion resistance – a key requirement for FRP equipment in many industrial applications. Fire retardance is achieved through the incorporation of bromine into the polymer backbone as shown in Figure 6. The bromine functionality not only provides superior fire retardance, but it also enhances the resin's resistance to corrosion in sodium hypochlorite (bleach) service. Brominated epoxy vinyl ester resins additionally deliver enhanced FRP toughness and fatigue resistance over standard epoxy vinyl ester resins.



n = 1 to 3

Figure 6. Brominated Epoxy Vinyl Ester Resin Structure

SUMMARY

Resin chemistry is the key to FRP performance in any environment, especially where chemical resistance is required. Early chemical-resistant polyester resins while superior to many metal alloy alternatives had problems with mechanical and thermal stress which can be directly attributed to their chemical structure. With an unusual combination of chemical resistance and toughness, epoxy vinyl ester resins have come to dominate the chemical-resistant resin market for FRP. Knowledge of resin chemistry is the key to understanding why different resin chemistries are required for different environments.