

## 4.4 Polyester Resin Plastic Products Fabrication

### 4.4.1 General Description<sup>1-2</sup>

A growing number of products are fabricated from liquid polyester resin reinforced with glass fibers and extended with various inorganic filler materials such as calcium carbonate, talc, mica, or small glass spheres. These composite materials are often referred to as fiberglass-reinforced plastic (FRP), or simply "fiberglass". The Society Of The Plastics industry designates these materials as "reinforced plastics/composites" (RP/C). Also, advanced reinforced plastics products are now formulated with fibers other than glass, such as carbon, aramid, and aramid/carbon hybrids. In some processes, resin products are fabricated without fibers. One major product using resins with fillers but no reinforcing fibers is the synthetic marble used in manufacturing bathroom countertops, sinks, and related items. Other applications of nonreinforced resin plastics include automobile body filler, bowling balls, and coatings.

Fiber-reinforced plastics products have a wide range of application in industry, transportation, home, and recreation. Industrial uses include storage tanks, skylights, electrical equipment, ducting, pipes, machine components, and corrosion resistant structural and process equipment. In transportation, automobile and aircraft applications are increasing rapidly. Home and recreational items include bathroom tubs and showers, boats (building and repair), surfboards and skis, helmets, swimming pools and hot tubs, and a variety of sporting goods.

The thermosetting polyester resins considered here are complex polymers resulting from the cross-linking reaction of a liquid unsaturated polyester with a vinyl type monomer, list often styrene. The unsaturated polyester is formed from the condensation reaction of an unsaturated dibasic acid or anhydride, a saturated dibasic acid or anhydride, and a polyfunctional alcohol. Table 4.4-1 lists the most common compounds used for each component of the polyester "backbone", as well as the principal cross-linking monomers. The chemical reactions that form both the unsaturated polyester and the cross-linked polyester resin are shown in Figure 4.4-1. The emission factors presented here apply to fabrication processes that use the finished liquid resins (as received by fabricators from chemical manufacturers), and not to the chemical processes used to produce these resins. (See Chapter 6, Organic Chemical Process Industry.)

In order to be used in the fabrication of products, the liquid resin must be mixed with a catalyst to initiate polymerization into a solid thermoset. Catalyst concentrations generally range from 1 to 2 percent by original weight of resin; within certain limits, the higher the catalyst concentration, the faster the cross-linking reaction proceeds. Common catalysts are organic peroxides, typically methyl ethyl ketone peroxide or benzoyl peroxide. Resins may contain inhibitors, to avoid self-curing during resin storage, and promoters, to allow polymerization to occur at lower temperatures.

The polyester resin/fiberglass industry consists of many small facilities (such as boat repair and small contract firms) and relatively few large firms that consume the major fraction of the total resin. Resin usage at these operations ranges from less than 5,000 kilograms per year (11,000 pounds) to over 3 million kilograms (6.6 million pounds) per year.

Reinforced plastics products are fabricated using any of several processes, depending on their size, shape, and other desired physical characteristics. The principal processes include hand layup,

Table 4.4-1. TYPICAL COMPONENTS OF RESINS

To Form The Unsaturated Polyester		
Unsaturated Acids	Saturated Acids	Polyfunctional Alcohols
Maleic anhydride Fumaric acid	Phthalic anhydride Isophthalic acid Adipic acid	Propylene glycol Ethylene glycol Diethylene glycol Dipropylene glycol Neopentyl glycol Pentaerythritol
Cross-Linking Agents (Monomers)		
Styrene Methyl methacrylate Vinyl toluene Vinyl acetate Diallyl phthalate Acrylamide 2-Ethyl hexylacrylate		

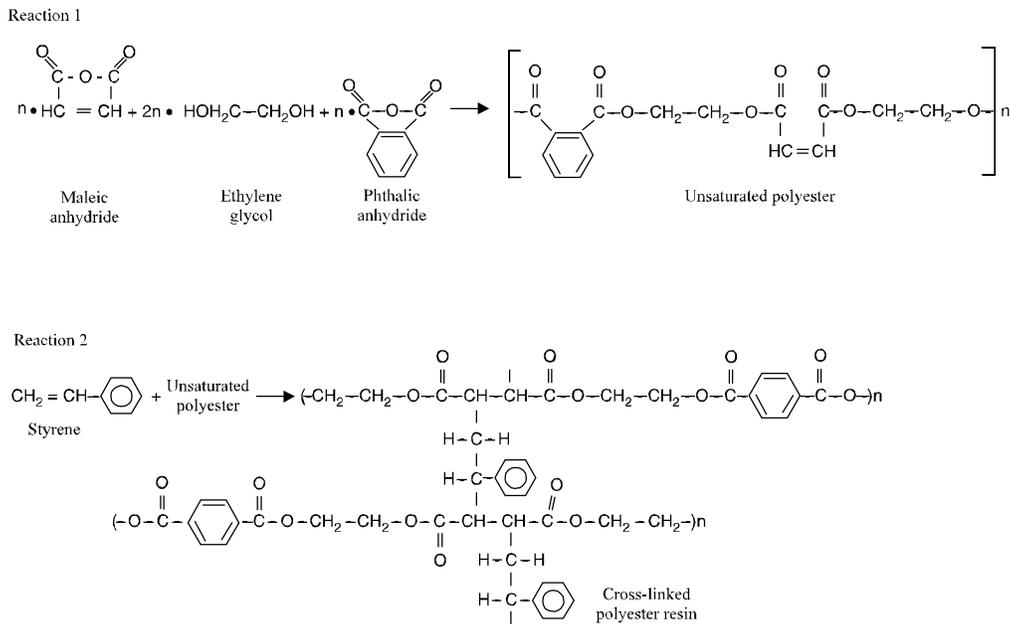


Figure 4.4-1. Typical reactions for unsaturated polyester and polyester resin formation.

spray layup (sprayup), continuous lamination, pultrusion, filament winding, and various closed molding operations.

Hand layup, using primarily manual techniques combined with open molds, is the simplest of the fabrication processes. Here, the reinforcement is manually fitted to a mold wetted with catalyzed resin mix, after which it is saturated with more resin. The reinforcement is in the form of either a chopped strand mat, a woven fabric, or often both. Layers of reinforcement and resin are added to build the desired laminate thickness. Squeegees, brushes, and rollers are used to smooth and compact each layer as it is applied. A release agent is usually first applied to the mold to facilitate removal of the composite. This is often a wax, which can be treated with a water soluble barrier coat such as polyvinyl alcohol to promote paint adhesion on parts that are to be painted. In many operations, the mold is first sprayed with gel coat, a clear or pigmented resin mix that forms the smooth outer surface of many products. Gel coat spray systems consist of separate sources of resin and catalyst, with an airless hand spray gun that mixes them together into an atomized resin/catalyst stream. Typical products are boat hulls and decks, swimming pools, bathtubs and showers, electrical consoles, and automobile components.

Spray layup, or "sprayup", is another open mold process, differing from hand layup in that it uses mechanical spraying and chopping equipment for depositing the resin and glass reinforcement. This process allows a greater production rate and more uniform parts than does hand layup, and often uses more complex molds. As in hand layup, gel coat is frequently applied to the mold before fabrication to produce the desired surface qualities. It is common practice to combine hand layup and sprayup operations.

For the reinforced layers, a device is attached to the sprayer system to chop glass fiber "roving" (uncut fiber) into predetermined lengths and project it to merge with the resin mix stream. The stream precoats the chop, and both are deposited simultaneously to the desired layer thickness on the mold surface (or on the gel coat that was applied to the mold). Layers are built up and rolled out on the mold as necessary to form the part. Products manufactured by sprayup are similar to those made by hand layup, except that more uniform and complex parts can generally be produced more efficiently with sprayup techniques. However, compared to hand layup, more resin generally is used to produce similar parts by spray layup because of the inevitable overspray of resin during application.

Continuous lamination of reinforced plastics materials involves impregnating various reinforcements with resins on an in-line conveyor. The resulting laminate is cured and trimmed as it passes through the various conveyor zones. In this process, the resin mix is metered onto a bottom carrier film, using a blade to control thickness. This film, which defines the panel's surface, is generally polyester, cellophane, or nylon and may have a smooth, embossed, or matte surface. Methyl methacrylate is sometimes used as the cross-linking agent, either alone or in combination with styrene, to increase strength and weather resistance. Chopped glass fibers free-fall into the resin mix and are allowed to saturate with resin, or "wet out". A second carrier film is applied on top of the panel before subsequent forming and curing. The cured panel is then stripped of its films, trimmed, and cut to the desired length. Principal products include translucent industrial skylights and greenhouse panels, wall and ceiling liners for food areas, garage doors, and cooling tower louvers. Figure 4.4-2 shows the basic elements of a continuous laminating production line.

Pultrusion, which can be thought of as extrusion by pulling, is used to produce continuous cross-sectional lineals similar to those made by extruding metals such as aluminum. Reinforcing fibers are pulled through a liquid resin mix bath and into a long machined steel die, where heat initiates an exothermic reaction to polymerize the thermosetting resin matrix. The composite profile emerges from

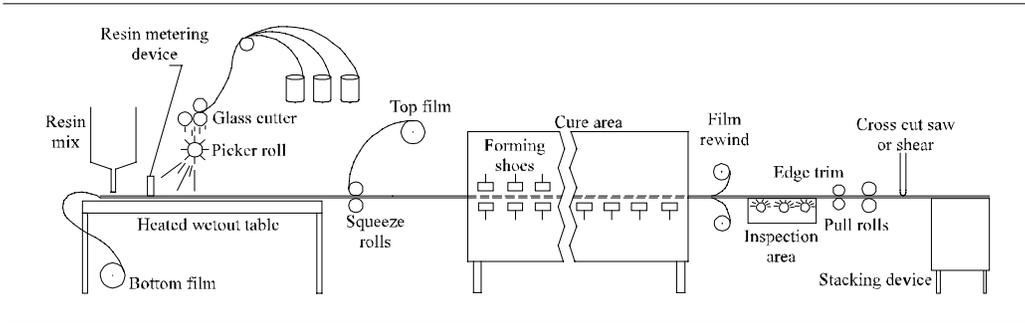


Figure 4.4-2. Typical continuous lamination production process.<sup>2</sup>

the die as a hot, constant cross-sectional that cools sufficiently to be fed into a clamping and pulling mechanism. The product can then be cut to desired lengths. Example products include electrical insulation materials, ladders, walkway gratings, structural supports, and rods and antennas.

Filament winding is the process of laying a band of resin impregnated fibers onto a rotating mandrel surface in a precise geometric pattern, and curing them to form the product. This is an efficient method of producing cylindrical parts with optimum strength characteristics suited to the specific design and application. Glass fiber is most often used for the filament, but aramid, graphite, and sometimes boron and various metal wires may be used. The filament can be wetted during fabrication, or previously impregnated filament ("prepreg") can be used. Figure 4.4-3 shows the filament winding process, and indicates the 3 most common winding patterns. The process illustration depicts circumferential winding, while the 2 smaller pictures show helical and polar winding. The various winding patterns can be used alone or in combination to achieve the desired strength and shape characteristics. Mandrels are made of a wide variety of materials and, in some applications, remain inside the finished product as a liner or core. Example products are storage tanks, fuselages, wind turbine and helicopter blades, and tubing and pipe.

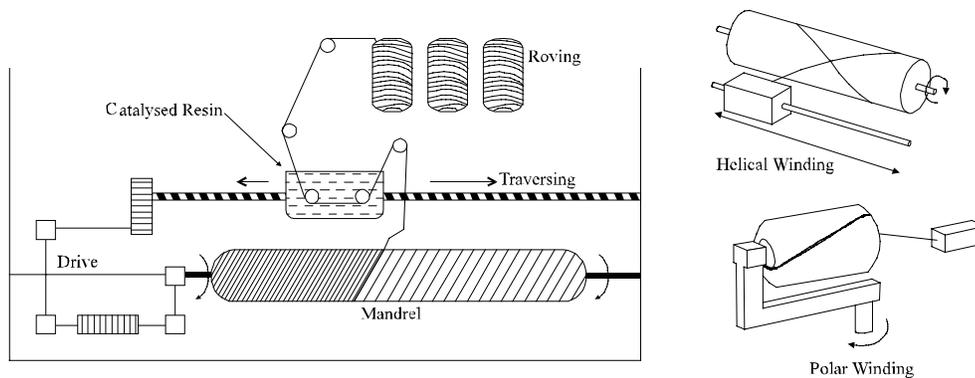


Figure 4.4-3. Typical filament winding process.<sup>3</sup>

Closed, such as compression or injection, molding operations involve the use of 2 matched dies to define the entire outer surface of the part. When closed and filled with a resin mix, the matched die mold is subjected to heat and pressure to cure the plastic. For the most durable production configuration, hardened metal dies are used (matched metal molding). Another closed

molding process is vacuum or pressure bag molding. In bag molding, a hand layup or sprayup is covered with a plastic film, and vacuum or pressure is applied to rigidly define the part and improve surface quality. The range of closed molded parts includes tool and appliance housings, cookware, brackets and other small parts, and automobile body and electrical components.

Synthetic marble casting, a large segment of the resin products industry, involves production of bathroom sinks, vanity tops, bathtubs, and accessories using filled resins that have the look of natural marble. No reinforcing fibers are used in these products. Pigmented or clear gel coat can either be applied to the mold itself or sprayed onto the product after casting to simulate the look of natural polished marble. Marble casting can be an open mold process, or it may be considered a semiclosed process if cast parts are removed from a closed mold for subsequent gel coat spraying.

#### 4.4.2 Emissions And Controls

Organic vapors consisting of volatile organic compounds (VOC) are emitted from fresh resin surfaces during the fabrication process, and from the use of solvents (usually acetone) for cleanup of hands, tools, molds, and spraying equipment. Cleaning solvent emissions can account for over 36 percent of the total plant VOC emissions.<sup>4</sup> There also may be some release of particulate emissions from automatic fiber chopping equipment, but these emissions have not been quantified.

Organic vapor emissions from polyester resin/fiberglass fabrication processes occur when the cross-linking agent (anomer) contained in the liquid resin evaporates into the air during resin application and curing. Styrene, methyl methacrylate, and vinyl toluene are 3 of the principal monomers used as cross-linking agents. Styrene is by far the most common. Other chemical components of resins are emitted only at trace levels because they not only have low vapor pressures, but also are substantially converted to polymers.<sup>5-6</sup>

Since emissions result from evaporation of monomer from the uncured resin, they depend upon the amount of resin surface exposed to the air and the time of exposure. Thus, the potential for emissions varies with the manner in which the resin is mixed, applied, handled, and cured. These factors vary among the different fabrication processes. For example, the spray layup process has the highest potential for VOC emissions because the atomization of resin into a spray creates an extremely large surface area from which volatile monomer can evaporate. By contrast, the emission potential in synthetic marble casting and closed molding operations is considerably lower because of the lower anomer content in the casting resins (30 to 38 percent, versus about 43 percent) and the enclosed nature of these molding operations. It has been found that styrene evaporation increases with increasing gel time, wind speed, and ambient temperature, and that increasing the hand rolling time on a hand layup or sprayup results in significantly higher styrene losses.<sup>1</sup> Thus, production changes that lessen the exposure of fresh resin surfaces to the air should be effective in reducing these evaporation losses.

In addition to production changes, resin formulation can be varied to affect the VOC emission potential. In general, a resin with lower monomer content should produce lower emissions. Evaluation tests with low-styrene emission laminating resins having a 36-percent styrene content found a 60- to 70-percent decrease in emission levels, compared to conventional resins (43 percent styrene), with no sacrifice in the physical properties of the laminate.<sup>7</sup> Vapor suppressing agents also are sometimes added to resins to reduce VOC emissions. Most vapor suppressants are paraffin waxes, stearates, or polymers of proprietary composition, constituting up to several weight percent of the mix. Limited laboratory and field data indicate that vapor suppressing resins reduce styrene losses by 30 to 70 percent.<sup>7-8</sup>

Emission factors for several fabrication processes using styrene content resins have been developed from the results of facility source tests (B Rating) and laboratory tests (C Rating), and through technology transfer estimations (D Rating).<sup>1</sup> Industry experts also provided additional information that was used to arrive at the final factors presented in Table 4.4-2.<sup>6</sup> Since the styrene content varies over a range of approximately 30 to 50 weight percent, these factors are based on the quantity of styrene monomer used in the process, rather than on the total amount of resin used. The factors for vapor-suppressed resins are typically 30 to 70 percent of those for regular resins. The factors are expressed as ranges because of the observed variability in source and laboratory test results and of the apparent sensitivity of emissions to process parameters.

Emissions should be calculated using actual resin monomer contents. When specific information about the percentage of styrene is unavailable, the representative average values in Table 4.4-3 should be used. The sample calculation illustrates the application of the emission factors.

#### Sample Calculation -

A fiberglass boat building facility consumes an average of 250 kg per day of styrene-containing resins using a combination of hand layup (75%) and spray layup (25%) techniques. The laminating resins for hand and spray layup contain 41.0 and 42.5 weight percent, respectively, of styrene. The resin used for hand layup contains a vapor-suppressing agent.

From Table 4.4-2 the weight percent of monomer emitted for hand layup using a vapor-suppressed resin is 2 - 7 (0.02 to 0.07 fraction of total styrene emitted); the factor for spray layup is 9 - 13 (0.09 to 0.13 fraction emitted). Assume the midpoints of these emission factor ranges (0.045 and 0.11, respectively).

Total VOC emissions are:

$$(250 \text{ kg/day}) [(0.75)(0.410)(0.045) + (0.25)(0.425)(0.11)] = 6.4 \text{ kg/day.}$$

Emissions from use of gel coat would be calculated in the same manner. If the monomer content of the resins were unknown, a representative value of 43 percent could be selected from Table 4.4-3 for this process combination. It should be noted that these emissions represent evaporation of styrene monomer only, and not of acetone or other solvents used for cleanup.

In addition to process changes and materials substitution, add-on control equipment can be used to reduce vapor emissions from styrene resins. However, control equipment is infrequently used at RP/C fabrication facilities, due to low exhaust VOC concentrations and the potential for contamination of adsorbent materials. Most plants use forced ventilation techniques to reduce worker exposure to styrene vapors, but vent the vapors directly to the atmosphere with no attempt at collection. At 1 continuous lamination facility where incineration was applied to vapors vented from the impregnation table, a 98.6 percent control efficiency was measured.<sup>1</sup> Carbon adsorption, absorption, and condensation have also been considered for recovering styrene and other organic vapors, but these techniques have not been applied to any significant extent in this industry.

Emissions from cleanup solvents can be controlled through good housekeeping and use practices, reclamation of spent solvent, and substitution with water-based solvent substitutes.

Table 4.4-2. EMISSION FACTORS FOR UNCONTROLLED POLYESTER RESIN PRODUCT FABRICATION PROCESSES<sup>a</sup>

(weight % of starting monomer emitted)

Process	Resin		EMISSION FACTOR RATING	Gel Coat		EMISSION FACTOR RATING
	NVS	VS <sup>b</sup>		NVS	VS <sup>b</sup>	
Hand layup	5 - 10	2 - 7	C	26 - 35	8 - 25	D
Spray layup	9 - 13	3 - 9	B	26 - 35	8 - 25	B
Continuous lamination	4 - 7	1 - 5	B	— <sup>c</sup>	— <sup>c</sup>	—
Pultrusion <sup>d</sup>	4 - 7	1 - 5	D	— <sup>c</sup>	— <sup>c</sup>	—
Filament winding <sup>e</sup>	5 - 10	2 - 7	D	— <sup>c</sup>	— <sup>c</sup>	—
Marble casting	1 - 3	1 - 2	B	— <sup>f</sup>	— <sup>f</sup>	—
Closed molding <sup>g</sup>	1 - 3	1 - 2	D	— <sup>c</sup>	— <sup>c</sup>	—

<sup>a</sup> Reference 9. Ranges represent the variability of processes and sensitivity of emissions to process parameters. Single value factors should be selected with caution. NVS = nonvapor-suppressed resin. VS = vapor-suppressed resin.

<sup>b</sup> Factors are 30 - 70% of those for nonvapor-suppressed resins.

<sup>c</sup> Gel coat is not normally used in this process.

<sup>d</sup> Resin factors for the continuous lamination process are assumed to apply.

<sup>e</sup> Resin factors for the hand layup process are assumed to apply.

<sup>f</sup> Factors unavailable. However, when cast parts are subsequently sprayed with gel coat, hand and spray layup gel coat factors are assumed to apply.

<sup>g</sup> Resin factors for marble casting, a semiclosed process, are assumed to apply.

Table 4.4-3. TYPICAL RESIN STYRENE PERCENTAGES

Resin Application	Resin Styrene Content <sup>a</sup> (wt. %)
Hand layup	43
Spray layup	43
Continuous lamination	40
Filament winding	40
Marble casting	32
Closed molding	35
Gel coat	35

<sup>a</sup> May vary by at least  $\pm 5$  percentage points.

#### References For Section 4.4

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