REFERENCE HANDBOOK

Introduction to Composites

FOURTH EDITION

composites institute

A NOTE ABOUT THE COMPOSITES INSTITUTE

The Composites Institute is a trade association of nearly 400 member companies.

The Composites Institute's mission is three-fold:

1. To grow the market for composites
2. To be the first source of information about composites
3. To support fair and equitable regulations consistent with science.

All of CI's activities center around this basic mission.

Conference/Trade shows/Meetings: For more than fifty years, the Composites Institute has sponsored a premier composites conference and exposition, the International Composites EXPO. ICE includes sessions on marketing, technical and regulatory issues, hands-on demonstrations and a world-class trade show. The Annual Management Meeting (AMM) occurs every summer at the Greenbrier Resort in White Sulphur Springs, West Virginia, and is a two-day summit for upper management and executives in the composites industry.

Market Expansion: CI's market development activities center around the Market Development Alliance, the Pultrusion Industry Council, and a host of other dynamic councils and task groups that address market- or product-specific issues.

Technical/Regulatory: This CI function represents industry to OSHA, EPA, and states on regulatory issues; informs industry on regulatory impacts and compliance strategies; manages cooperative industry regulatory programs; and represents industry to ASTM, ISO, NFPA, and other codes and standards organizations.

SMC Automotive Alliance: The SMCAA disseminates information and develops practices that promote the benefits and uses of SMC in the automotive industry, while ensuring that SMC is responsibly applied with regard to the environment and safety of the industry and public.

Who's Who at the Composites Institute

EXECUTIVE
Catherine Randazzo, Executive Director, 212-351-5405, e-mail: crandazz@socplas.org
Tara Miller, Assistant to the Executive Director, 212-351-5406, e-mail: tmiller@socplas.org

CONFERENCE/TRADE SHOWS/MEETINGS
Peggy Stabach, Conference & Exposition manager, 212-351-5404, e-mail: pstabach@socplas.org
Hope Downie, Meeting Planner, 212-351-5428, e-mail: hdownie@socplas.org

MARKET DEVELOPMENT
John Busel, Manager, 212-351-5413, e-mail: jbusel@socplas.org
Doug Barno, Consulting Director, 614-587-1444, e-mail: dsbarno@aol.com

TECHNICAL/REGULATORY
John Schweitzer, Technical Director, 313-668-4703, e-mail: jschweit@aol.com

SMC AUTOMOTIVE ALLIANCE
Erin Millerschin, Program Director, 248-649-4888, emillers@socplas.org

For more information, you may write us at 355 Lexington Avenue, New York, NY 10017, phone us at 212-351-5410, fax us at 212-370-1731 or visit our website at www.socplas.org.

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Introduction to Composites

Chapter 1

Polymers in Our Lives for Good

The world we live in is filled with examples of how polymers have changed our lives. One of the largest families within the category of polymers are the materials we know as "plastics" and those who are familiar with composites will recognize polymers by another common name – "resins."

Every day, more manufacturers and consumers turn to plastics as a source of high quality, durable, cost-effective products. Applications from snowboards and bicycles to the bridge decking over our highways and the body panels on cars are very much a part of our everyday experience.

One of many sporting good applications on the market today

Plastics are, for the most part, products of man's ingenuity and continuing technological breakthroughs. And there are many different kinds of plastics. The names of some are familiar, such as nylon, polyester and polyethylene. Other resins, such as epoxies, phenolics, bisphenols or silicones may not be as recognizable to the average person. Some successful plastics are composed of the resin only, while others are complex mixtures of reinforcements, additives and other ingredients. However, each of the basic plastic resins is a full-fledged member of the "family of plastics."

Finding the Answers in Plastics

Most businesses today are experiencing increased competition. More than at any other time in history, rapid changes in technology and shifting markets affect industry after industry. Additional concerns such as increased international competition and environmental and social issues commonly impact everyday business decisions.

In this dynamic and changing business climate plastics in general and composites in particular have proven to be extremely effective in reducing cost, improving productivity or solving product problems. The many attractive benefits of these materials have fueled the growth of new application development in markets as diverse as transportation, consumer products, construction, appliances and business equipment, aerospace/defense and others. There is hardly a product or market that does not represent an opportunity for the creative use of plastics.

Composites

Composites are a polymer matrix, either thermoset or thermoplastic, reinforced with a fiber or other material with a sufficient aspect ratio (length to thickness) to provide a discernible reinforcing function in one or more directions. Not all plastics are composites. In fact, the majority of plastic materials today are pure plastic and not some form of composite. Many products such as toys, decorative products, household goods and similar applications require only the strength of the plastic resin to perform their functions. "Engineering-grade" thermoplastics can offer improved performance characteristics, such as increased heat distortion temperatures, but usually at a higher cost than general-purpose plastic resins. When additional strength is needed, many types of plastics can be reinforced with structural materials – usually reinforcing fibers – to meet the demands for higher performance. Any thermoplastic or thermoset plastic resin that is reinforced is considered a composite.

Over the years, the term fiberglass reinforced plastics (FRP) has become almost synonymous with fiberglass reinforced polyesters (also known as FRP), glass fiber reinforced plastic (GRP), reinforced plastics (RP) and similar alphabetical designations. For the purposes of this introduction to the discipline, we will use the term "composite" to identify any reinforced plastic material, whether thermoplastic or thermosetting, which is reinforced by fiber or other materials and which may have additional functional components or ingredients. Composites is the approved designation of the SPI Composites Institute. Use of the term "composites" to describe the materials covered in this course is encouraged.

Thermoplastic vs. Thermoset

Most plastics, and virtually all unreinforced plastics, are "thermoplastic" by nature. Thermoplastic materials become soft when heated and may be shaped or reshaped while in a heated semi-fluid state. When the plastic cools, the new, molded shape is retained. If another shape is desired, thermoplastic materials may even be reheated and remolded. Think of the processing characteristics of thermoplastics as being more like paraffin wax – you may heat the wax until it softens, pour the liquid wax into a mold and cool it. The wax will take the shape of the mold. If reheated, the wax can be molded into a different shape. Thermoplastics are similar in nature to this heat-to-soften characteristic.

Most reinforced plastics are thermosetting. Thermosetting resins are normally liquids, or in a few special cases, solids with low melting point temperatures. Engineered reactions involving chemicals and heat, which occur during processing, cause these thermosetting resins to become solids. Generally, a thermosetting reaction cannot be reversed. In this sense, thermosetting resins are much like an egg. Once heated or cooked, the egg cannot be changed back into its original liquid form or put back in the shell after hardening. The change is permanent.

When thermosetting resins are reinforced with appropriate materials, they become among the strongest materials for their weight which technology has ever developed. In addition, reinforced thermoplastic resins are enjoying increased popularity. Many performance properties available a few years ago only in reinforced thermosets are now available in reinforced thermoplastics.

Building Composites Knowledge

This book and companion workshop "Introduction to Composites," have been designed so that your knowledge of composites, and your confidence, will grow as you become more familiar with these materials. The content has been developed as a primer intended for engineers, designers, manufacturers, marketers and others who may be unfamiliar with composites.

Chapter 1 is devoted to understanding the markets for composites and the end-use applications which make up the major commercial segments of the industry. You will also find explanations for each composite performance benefit and a summary of the characteristics of composites which help to make composites the material of choice for so many applications.

Chapter 2 deals with the major materials which comprise composites. These materials include:

- Polymers (general)
- Thermosetting resins
- Thermoplastic resins
- Reinforcements
- Additives
- Fillers
- Materials interaction and the importance of "systems" in application development

Chapter 3 focuses on composite manufacturing processes. Over a dozen commonly used processes are described, compared and the advantages/disadvantages identified. Important process considerations are highlighted to assist in understanding and selecting the appropriate fabricating process.

Chapter 4 offers proven, effective approaches to composite design. Economic considerations and future direction of the industry are also covered in the balance of this chapter.

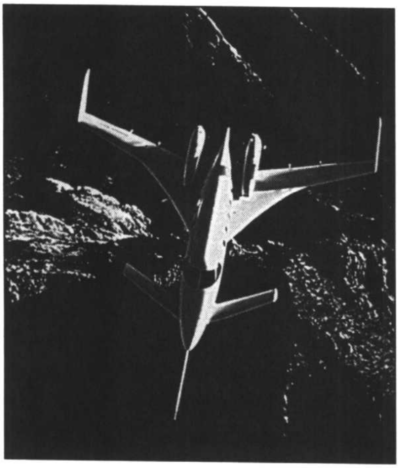
At the conclusion of the book, you will find a glossary of the terms which are commonly used in the composite industry.

Market Overview and Applications

Because composites are widely used in many different applications, the SPI Composites Institute recognizes, and regularly tracks, nine major commercial segments of the market.

All composites applications can be found within one of these market segments. Table 1.1 (page 5) shows composite shipments by market segment for the last three years. On page 6, each segment's share of the total composites market is displayed in the pie chart. What kinds of products do these market segments contain? With literally thousands of composite applications in production, it would not be practical to list all end-uses. A sampling of products by major application may be helpful in understanding the character of the industry:

Aircraft/Aerospace/Defense: includes all composite materials used in commercial, pleasure or military aircraft such as flight surfaces, cabin interiors and accessories, heat shields, components and rocket motor casings for aerospace and related applications. Also military helmets, armament, rocket launchers, etc.



First all-composite commercial airplane

Appliance/Business Equipment: includes composites used in appliances such as refrigerators, ranges, freezers, microwave ovens, small household appliances, power tools, as well as business and office equipment such as calculators, copiers, computers and similar end-uses.

Construction: includes materials for building trades including swimming pools, concrete pouring forms, gutters and downspouts, cooling tower components, highway signs, shower stalls, bathtubs, lavatories, spas, whirlpools, paneling for greenhouses, patios, etc. Construction applications such as bridge decks and components, dowel bars, rebar and piling are also in this category.

Consumer Products: includes sports and recreational equipment such as fishing rods, skis, snowboards, golf clubs, snowmobiles, bowling equipment, mobile campers, swimming pool accessories and equipment, bicycles, exercise equipment, serving trays, lamp shades, boxes and containers, countertops, seating, furniture, and microwave cookware.

Corrosion-Resistant Equipment: includes products for chemical-resistant service including pipe and fittings, tanks, stacks, ducts and hoods, pumps, fans, containers, filtration equipment, oil field sucker rods, grating, and related products for the oil and gas, chemical processing industry and water/wastewater treatment markets.

Electrical/Electronic: includes components for electrical and electronic applications including rods, tubes, molded parts, pole line hardware, substation equipment, electronic microwave antennas, electronic connections, printed wiring boards, injection molded
boards, and polyester-based panel boards, housings and circuit breaker boxes.

Marine: includes composite materials used in commercial, pleasure and naval boats and ships. Includes hardware and components like motor covers, moorings, marine docks, buoys, floats, canoes, kayaks, personal watercraft and car-top boats.

Transportation: includes parts for automobiles such as front-end assemblies, body panels, grill opening panels, fender liners, tail light housings, instrument panels, springs, driveshafts and heater housings; truck cabs, wind deflectors, trailer body paneling, railroad rolling stock, boxcar doors, refrigerator car liners, subway car seats and components, tractor parts, scooters, tank truck and similar products.

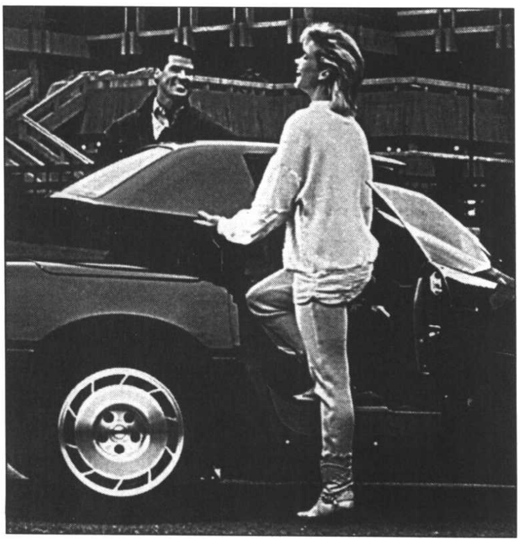
Why Use Composites?

Composites have come of age due to the widespread recognition and acceptance among engineers, designers, manufacturers and management of the unique combinations of performance benefits which these materials offer. Composite features translate into multiple benefits for manufacturers and consumers alike. By better understanding the benefits of composites, designers, engineers, and others associated with turning design concepts into product realities can make their jobs easier and more effective.

In any successful composites application, one or more of the following benefits will normally be at work:

1. High Strength – Composites are among the most effective materials in delivering high strength. These materials can be designed to provide a wide range of mechanical properties including tensile, flexural, impact and compressive strength. Unlike traditional materials, composites can have their strengths oriented or tailored to meet specific design requirements of an application.

2. Light Weight – Composites deliver more strength per unit of weight than unreinforced plastics, as well as most metals. This combination of high strength/light weight is a powerful incentive for the effective use of composites.



Light weight is just one of the many benefits of composites

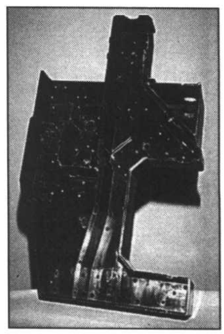
3. Design Flexibility – Composites can be formed into virtually any shape a designer may have in mind: complex or simple, large or small, structural or appearance, decorative or functional. With composites, many choices are available without having to make costly trade-offs. In addition, composites free designers to try new approaches, from prototype to production.

4. Dimensional Stability – Under severe mechanical and environmental stresses, thermoset composites maintain their shape and functionality. Typically, composites do not exhibit the viscoelastic or "cold-creep" characteristics of unreinforced thermoplastics. The coefficient of thermal expansion is reduced. Generally speaking, the yield point of a composite is its break point.

5. High Dielectric Strength – Composites have outstanding electrical insulating properties, making them obvious choices for current carrying components. It is also possible to impart electrical conductivity to composites through the use of appropriate modifiers and additives, if this is required by the application.

6. Corrosion Resistance – Composites do not rust or corrode. There are a number of resin systems available which provide long-term resistance to nearly every chemical and temperature environment. Properly designed composite parts have long service life and minimum maintenance as well.

7. Parts Consolidation – Composite moldings often replace assemblies of many parts and fasteners required for traditional materials such as steel. This can reduce manufacturing cost and frequently results in a better, more trouble-free part.



An optics bench such as this is a prime example of parts consolidation

8. Finishing – In many composite applications, color can be molded into the product for long lasting, minimum maintenance appearance. Low-profile and low-shrink resin systems are compatible with most metallic painting operations. Proper design of molds and choice of materials can reduce trim waste, flash, sanding and other post-molding operations.

9. Low Tooling Cost – As a general rule, regardless of the processing methods selected, tooling costs for composites can be lower than tooling costs and associated finishing costs for traditional materials such as steel, aluminum, alloys, and other materials.

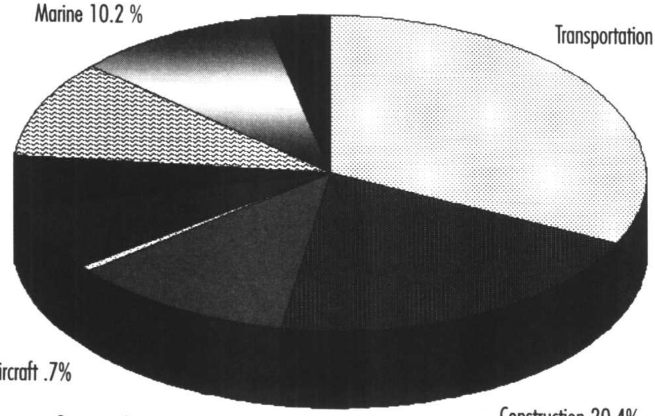
10. Proven History of Successful Applications – In the last 45 years, over 50,000 successful composite applications have helped to prove the value of these amazing materials. Where once the pioneers of the industry struggled to blaze a trail for composite materials acceptance, today's engineers, designers and marketing professionals can point with confidence to a growing array of end uses and applications. These applications testify to the cost and performance benefits of composites.

U.S. Composites Shipments by Market Segment

(Units: Millions of pounds)

Markets	1995	1996	Projected 1997
Aircraft/Aerospace/Military	23.7	23.7	23.9
Appliance/Business Equipment	166.6	176.9	184.3
Construction	629.3	655.1	696.2
Consumer Products	184.0	194.2	226.0
Corrosion-Resistant Equipment	394.4	381.1	389.0
Electrical/Electronic	314.8	318.8	339.0
Marine	372.0	367.9	359.8
Transportation	981.8	998.5	1091.1
Other	106.7	107.3	111.2
TOTAL	3173.3	3223.5	3420.5

1997 Semi-Annual Statistical Report



Source: SPI Composites Institute
Includes: Reinforced Thermoset Resin, Materials, Reinforcements and Fillers

Summary

The composites industry has developed and matured into a major provider of products, producing billions of pounds of materials per year to satisfy the demands of even the toughest applications. Increasingly, designers turn to composites to solve problems, improve productivity or create new products.

Should you need additional information, there are professionals prepared to answer your questions in areas such as reinforcements, resins, additives and fillers, processes, design, or other important considerations. You can fabricate your own parts, or work with a well-established national network of custom fabricators capable of providing composite parts molded to your design and specifications. The SPI Composites Institute will help you find a designer, molder or material supplier to assist you.

Introduction to Composites

Chapter 2

Understanding Composites

As you are already beginning to see, composites are an unusually versatile and valuable family of materials which can solve problems, improve productivity and facilitate the introduction of new products in your market or business. But there are a few tricks to understanding and applying composite technology to a new or existing product. The new things to learn are not difficult, but they are important. Like any new material, working with composites requires getting familiar with the basics.

Throughout Chapter 2, we will be studying the technology of the materials which comprise composites, including resins, reinforcements, fillers and additives. The final portion of this chapter deals with the important and interactive relationship between composite materials, processing and the functional requirements of the product.

It is important to remember that with certain materials, i.e., sheet steel, aluminum bar stock, magnesium die casting, etc., the fabrication process shapes the material into final product form without changing the basic properties of the materials themselves. This is not necessarily the case with composites. The properties and characteristics of composite materials are generally created at the same time that the product is being formed. In this way, composites are more like concrete than metals. That is, you create a concrete material system when the ingredients are mixed and allowed to set and cure.

There are great benefits inherent in the versatile family of composite materials. But, there can also be pitfalls if proper attention is not given to the initial design and testing phase, and if adequate materials, process and quality control procedures are not in place during manufacture. This requires knowledge of the materials and process in the design and evaluation phase of an application development to assure that the properties and benefits of composites have been optimized. Ineffective application of composite materials or processes may result in cost/performance disadvantages.

An additional benefit of working with composite materials is that models and prototypes can be produced which essentially duplicate the performance of the desired production part. This allows comprehensive testing of the design before commitment to manufacturing investment.

Resins

The resins which are used in composites are important ingredients in any successful application. Each resin offers a unique combination of performance properties, processability and cost. Understanding the relationship among the various resins helps users unlock the "power" of composites to solve problems, improve productivity, or create applications.

The Basics of Polymers

The term polymer comes from "poly" meaning many and "mer," describing a unit. Monomers are single building blocks that when joined together form polymers. All polymers commonly used in composites are the products of sophisticated chemical processing. Before entering the world of polymers, it is helpful to have an understanding of the chemistry involved. You don't have to be a chemist to understand these materials.

Chemists use a shorthand notation for various chemical elements. The significant elements which make up most of the plastics we will discuss here are:

C = carbon
H = hydrogen
O = oxygen

For example, using this shorthand, a typical polyester resin might be something like:

$H - (OOC\text{-}C_6H_4\text{-}COO\text{-}C_2H_4)n\text{-}OH$

In this case the structure inside the brackets repeats itself many times, as designated by the number n. For a polymer, this would be a long chain and the value for n could be greater than 100.

Using the same shorthand, styrene would be shown as:
$C_6H_5\text{-}CH = CH_2$

Thermoset vs. Thermoplastic

As you learned in Chapter 1, resins or plastics are divided into two major groups known as thermoset and thermoplastic. Thermoplastic resins become soft when heated, and may be shaped or molded while in a heated semifluid state. Thermoset resins, on the other hand, are usually liquids or low melting point solids in their initial form. When used to produce finished goods, these thermosetting resins are "cured" by the use of a catalyst, heat or a combination of the two. Once cured, solid thermoset resins cannot be converted back to their original liquid form. Unlike thermoplastic resins, cured thermosets will not melt and flow when heated and once formed they cannot be reshaped.

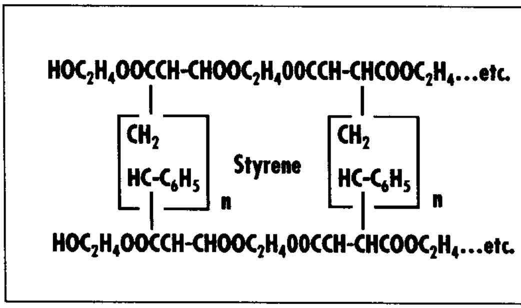
The composites industry has been divided into thermoset and thermoplastic camps primarily because of differing requirements of their fabrication processes. Both types of plastics can benefit from reinforcement. The initial growth of composites was in thermosets – primarily glass fiber reinforced unsaturated polyester resins. Recently, however, rapid growth has been occurring in the use of reinforced thermoplastics. This trend is expected to continue as thermoplastics improve in properties and cost effectiveness. Therefore, it is increasingly important that persons contemplating the use of composites be well versed in both thermosetting and thermoplastic polymers.

Thermosetting Resins

The most common thermosetting resins used in the composites industry are unsaturated polyesters, epoxies, vinyl esters, polyurethanes and phenolics. There are differences between these groups that must be understood to choose the proper material for a specific application.

Polyester Resins

Unsaturated polyester resins are the workhorse of the composites industry and they represent approximately 75% of the total resins used. To avoid any confusion in terms, readers should be aware that there is a family of thermoplastic polyesters which are best known for their use as fibers for textiles and clothing. These resins are also available, in a different grade, for injection molding of both composite and non-composite parts. Polyesters are produced by the condensation polymerization of dicarboxylic acids and diayoric alcohols (glycols). In addition, unsaturated polyesters contain an unsaturated material, such as maleic anhydride or fumaric acid, as part of the dicarboxylic acid component. The finished polymer is dissolved in a reactive monomer such as styrene to give a low viscosity liquid. When this resin is cured, the monomer reacts with the unsaturated sites on the polymer converting it to a solid thermoset structure.



Typical polyester schematic formula

There are many different acids and glycols used in polyester resins. Some of the common ones, and their reasons for use, are listed in the following two tables.

Glycols	Contributes
Propylene glycol	Water and chemical resistance
Ethylene glycol	Low cost, rigidity
Dipropylene glycol	Flexibility, toughness
Diethylene glycol	Flexibility, toughness
Neopentyl glycol	Ultraviolet, water and chemical resistance
Propoxylated Bisphenol A	Water and chemical resistance

Acids	Contributes
Phthalic anhydride	Low cost, styrene compatibility
Maleic anhydride	Unsaturation
Adipic acid	Flexibility, toughness
Isophthalic acid	High heat deflection temperature, strong water and chemical resistance
Terephthalic acid	High heat deflection point temperature, strong water and chemical resistance

A range of raw materials and processing techniques are available to achieve the desired properties in the formulated or processed polyester resin. Because polyesters are so versatile and because of their capacity to be modified or tailored during the building of the polymer chains, they have been found to have almost unlimited usefulness in all segments of the composites industry.

The principal advantage of these resins is a balance of properties (including mechanical, chemical, electrical), dimensional stability, cost and ease of handling or processing.

Unsaturated polyesters are divided into classes depending upon structures of their basic building blocks. Some common examples would be orthophthalic ("ortho"), isophthalic ("iso"), dicyclopentadiene ("DCPD") and bisphenol A fumarate resins. In addition, polyester resins are classified according to end use application as either general purpose (GP) or specialty polyesters.

General Purpose Polyesters

The term "general purpose" does not specify a particular polyester resin classification but instead it defines products that are relatively low in cost, offer good mechanical and electrical performance and a well-defined set of processing/fabricating characteristics. Almost all ortho and DCPD resins and some iso resins fall into the GP category.

Normally, GP polyesters are supplied with medium to low viscosities (similar to maple syrup or heavy motor oil) and typically require only the addition of catalyst and promoter. They may also be used in combination with fillers and additives to complete a processable resin system. GP polyesters are used in the open-mold processes (hand lay-up/spray-up, etc.) to produce a wide range of products including boats, truck components, furniture, tubs and showers and applications which do not require the premium performance of higher cost grades of polyester.

Specialty Polyesters

Because polyesters can be chemically tailored to meet the requirements of a wide range of applications, a number of specialty polyesters are available. The specialty polyesters include:

- Flexibilized polyesters
- Electrical grade polyesters
- Corrosion-resistant polyesters
- Heat resistant polyesters
- Fire retardant polyesters
- Translucent polyesters
- Low shrink/low profile polyesters

Specialty polyesters typically derive their performance from the chemical makeup of the polymer. The proper use of fillers or additives can also enhance properties like fire resistance, fatigue performance or chemical resistance. Improvements in one property such as chemical resistance, may also improve other properties, such as temperature resistance. Bisphenol A fumarate, for example, is used in fabrication because of its ability to tolerate a range of chemical exposure and higher in-service temperatures.

Liquid styrenated polyester resins can be easily shipped to fabricators who do the final shaping and curing into useful products. The mechanism for curing is a reaction between the unsaturation in the polyester and the styrene monomer. This results in the polyester chains being tied together by the styrene monomer.

The curing of polyester resins is much different than for epoxies, urethanes or phenolics. Most epoxies and urethanes begin to increase in viscosity as soon as they are catalyzed and continue to increase until they are cured. Polyesters provide a specific working time (gel time) with very little viscosity increase or temperature change. Gelation takes place when less than 5% of the original unsaturation has reacted, and full cure occurs *very quickly after this.*

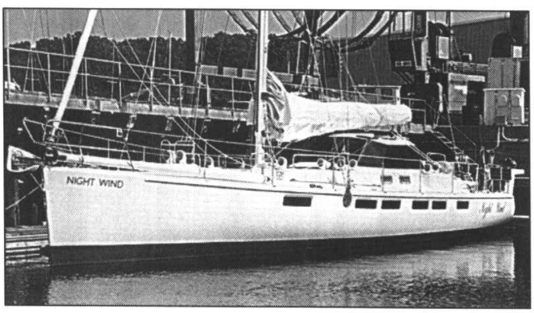
Please see Table 2.1 (page 13) for a guide to polyester resin selection. For additional information concerning polyesters, consult the *SPI Buyer's Guide* or your resin supplier.

Polyester producers have proved willing and capable of supplying resins with the necessary properties to meet the requirements of specific end use applications. These resins can be formulated and chemically tailored to provide properties and process compatibility.

Gel Coats

Gel coats are designed as an in-mold coating to provide cosmetic appeal to a composite part and to protect the part's substrate from the elements. Gel coats are designed to meet a wide range of product requirements, and are formulated for enhanced chalk and weather resistance, resistance to osmotic blister and tooling applications. The end use of gel coated composite parts ranges from marine applications to sanitary ware.

While the gel coat film is curing, but before the cure is complete, a fiberglass laminate made up of fiberglass and polyester resin is applied to the gel coat film for reinforcement.



Gel coats weather resistance and durability make them ideal for marine applications

Gel coats are available in pigmented and clear formulations in a variety of thermosetting resin systems. Color matching and quality control of color are now done with state of the art spectrophotometers and color matching computer software. The gel coat manufacturer chooses the gel coat resin type that will best meet the specifications of the composite part manufacturer.

Gel coats are manufactured using eight basic chemical component groups. In addition to the selected resin, gel coats also contain pigments, promoters, thixotropic agents, extenders (fillers), inhibitors, monomers and miscellaneous additives.

Resin types: the type of resin selected for a gel coat formula is dependent on the intended use of the composite part. Isophthalic (iso), and iso/neopentyl glycol resins are the predominant types of polyester resin used in making gel coat for the composites industry. Other resins are utilized to make flexible, fire retarding, tooling, chemical resistant, vinyl ester and other specialty gel coats.

Pigment selection: pigment selection is a key component in the manufacture of gel coat. Correct pigment selection is critical for obtaining opacity and the best available resistance to weathering and chalking. Gel coat manufacturers have been converting from lead and chromate-based pigments in their formulations to bring their gel coats into compliance with government guidelines and to be more environmentally friendly.

Thixotropes: thixotropic agents are low-weight additives (usually silica and organo-clays). Thixotropic agents enable the gel coat to flow during spray application and then hold on the molds vertical surfaces without sagging during cure.

Promoters and inhibitors: promoters and inhibitors control the gel coats gel and cure time. They allow the gel coat manufacturer to meet specific performance specifications relating to working time during the lay-up process.

Monomer and extenders: styrene monomer is one of the primary ingredients in most gel coat formulations to adjust viscosity and make the system easy to handle. Extenders are minerals that work in conjunction with thixotropic agents and dispersions. Extenders are used to help control gel coat viscosity, pigment suspension in the formula, improve opacity and enhance hydrolytic stability.

Miscellaneous additives: there are also a variety of additional miscellaneous additives used in gel coat to achieve specific performance characteristics. Wetting agents are used to enhance the performance of selected pigments. Ultraviolet (UV) absorbers are used to retard the destructive effects of UV radiation on the gel coat film. Other additives may be selected to overcome surface tension problems and to improve air release as the gel coat film cures.

Gel coated composite parts have become the product of choice where colorful, easily main-