







Performance Resins in Composites







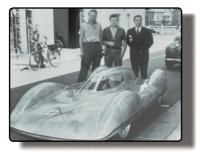






50 years of reliability, experience and innovation

The Crystic family of resins is at the heart of our success. In 1946 Scott Bader were the first UK company to manufacture unsaturated polyester resins in Europe. In 1953 the Crystic range of polyesters was introduced and its revolutionary applications have meant that Crystic has been the byword for superior technological achievement ever since.













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COMPOSITES HANDBOOK

Preface

The global nature of today's reinforced plastics industry creates a demand from all over the world, for basic background information. This sixteenth edition of the Composites Handbook provides an introduction to reinforced plastic in terms of basic chemistry, resins, reinforcements and application techniques. It also encompasses the major advances in material and process technologies which have occurred since the first edition was published in 1953.

The uniqueness of reinforced plastic lies in the fact that the material of construction and the end product are produced simultaneously, so quality control is a highly significant part of the process.

The general guidance, advice and technical data contained in this handbook is intended to help designers, moulders and end-users to realise the full potential of this unique material as a truly structural engineering plastic.

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Introduction

Plastics

The term "plastic" is used to describe the moulded form of a synthetic (i.e. man-made) resin. These resins are composed of large, chain-like molecules known as polymers, which also occur naturally as, for example, cellulose, protein and rubber. Most synthetic resins are made from chemicals derived from oil and it is these man-made polymers which are used to produce what are commonly known as "plastics".

Plastics in their various forms have existed since the late 19th century, but most of the materials referred to as plastics today have been developed during the past 50 years.

A large variety of plastics is now available and they exist in various physical forms. They can be bulk solid materials, rigid or flexible foams, or in the form of sheet or film. Most fall into one of two categories; thermoplastic or thermoset. Thermoplastics can be formed and re-formed by the use of heat (eg. polyethylene, PVC, etc.). Thermosets, on the other hand, harden by a chemical reaction, generating heat when they are formed and cannot be melted or re-formed (eg. unsaturated polyesters, epoxies, vinyl esters etc.).

The Nature of Reinforced Plastics

Reinforced Plastic is the generic term used to describe specific plastic materials reinforced with high strength fibres. Since their development, these materials have been commonly known by names such as "Fibreglass" and GRP (Glass Reinforced Plastic). Though GRP is still the most used term, the development and utilisation of fibres other than glass makes FRP (Fibre Reinforced Plastic) a more accurate and comprehensive description. Within the reinforced plastics industry itself, "Composite" is the term felt to best describe this light, durable and astonishingly tough constructional material.

Composites can be fabricated into a wide spectrum of products, from the purely decorative to complex, engineered structures. They may be translucent, opaque or coloured, thick or thin, flat or shaped and there is virtually no limit on size. Composites can be found in most areas of daily life, in the form of roof sheeting, tanks, pipes, vehicle bodies, buildings, boats, etc.

To produce a composite item, two basic components are required, these being a synthetic resin and a strong fibre. The resin, which could be a polyester, epoxy or vinyl ester, is normally supplied as a viscous liquid, which sets to a hard solid when suitably activated. The fibre may be glass, carbon, polyaramid, or a combination of some or all of these. What makes composites unique is the fact that the material of construction and the end product are produced simultaneously. Using a suitable mould, layers of fibre are impregnated with activated resin until the required thickness is achieved. When complete, the moulding is removed and the mould can then be re-used to produce more, identical items.

This handbook describes in detail the materials, techniques and applications of composite manufacture, and presents solutions to any problems that may arise.

MATERIALS

Resins

Several resin types are employed in the manufacture of composite products. All of these resins are thermosets but they differ in their chemical make-up, thus exhibiting diverse properties. This means that manufacturers can choose resins which enable them to tailor their products to meet specific requirements. This handbook is concerned mainly with Crystic* polyester resins, but other types such as vinyl ester, epoxy, DCPD, phenolic and also hybrid systems are described in this section.

Polyesters

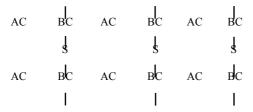
Crystic resins are unsaturated polyesters. The raw materials used for the manufacture of unsaturated polyester resins are oil based (see Figure 1) and to produce a polyester of this type, three basic chemical components are generally required :-

- A: saturated acid (e.g. phthalic anhydride)
- B: unsaturated acid (e.g. maleic anhydride)
- C: dihydric alcohol (e.g. propylene glycol)

With the application of heat, these chemicals combine to form a resin which is a viscous liquid when hot, but a brittle solid when cold. The term "polyester" is derived from the link between A or B with C, which is termed an "ester" link.

Whilst it is still hot, the resin is dissolved in a monomer which is usually styrene though others can be, and are, used. The monomer performs the vital function of enabling the resin to cure from a liquid to a solid, by crosslinking the molecular chains of the polyester. No by-products are evolved during this process, which means the resins can be moulded without the use of pressure. They are therefore known as contact or low pressure moulding resins. The molecular chains of the polyester can be represented as follows:

With the addition of styrene — S — and in the presence of a catalyst and accelerator, the styrene crosslinks the chains to form a highly complex three dimensional network as follows :



At this stage, the polyester resin is said to be cured. It is now a chemically resistant and (usually) hard solid. The cross-linking, or curing, process is called polymerisation and is a non-reversible chemical reaction.

Once cured, the resin will continue to 'mature', during which time the moulding will acquire its full properties. This process, which can take several weeks to complete at room temperature, can be accelerated by post curing the moulding at elevated temperatures (see Quality Control section).

Polyester resins with differing characteristics and properties are produced by manipulating the types and amounts of raw materials used in their manufacture (see "Properties" section).

DCPD Polyesters

The use of DCPD (Dicyclopentadiene) in unsaturated polyester resin manufacture was first introduced in the United States in the late 1970's. Since that time, its commercial use has developed and resins containing DCPD are now produced worldwide.

There are two basic methods of producing DCPD polyesters, as follows :-

Dow Hydrolysis Method

This method involves an initial reaction using three components :-

A: Maleic Anhydride

C: DCPD

These three components are reacted together at a temperature lower than 130° C, to produce what is known as an acid functionalised "end cap". A further reaction is then carried out, using the acid end cap and other standard polyester raw materials. During this reaction, the acid end cap attaches to the molecular chains of the polymer, thus restricting their length and thereby reducing the viscosity of the final product. This means that less styrene is needed to achieve a resin with a usable viscosity.

Up to 30% weight for weight DCPD can be added to a polyester (on solid resin) using this method.

Diels - Alder Reaction Method

This method allows up to 70% weight for weight DCPD to be used (on solid resin) in the manufacture of a polyester. It involves converting dicyclopentadiene (DCPD) to cyclopentadiene (CPD) at a temperature greater than 130°C. The CPD is then grafted onto the resin backbone by reaction with a site of unsaturation. This can be achieved by an early reaction with maleic anhydride or at a later stage of the polymerisation process.

These two processes are similar in that both reactions occur in both systems but in different ratios. The degree of each reaction type is controlled by temperature and water content in the first stage. The advantages of incorporating DCPD into polyester resins are lower styrene content, combined with good properties. The main disadvantage is the fact that DCPD solidifies at room temperature so heated storage and handling facilities are required.

Epoxy Resins

Epoxy resins have been commercially available since the early 1950's and are now used in a wide range of industries and applications.

Epoxies are classified in the plastics industry as thermosetting resins and they achieve the thermoset state by means of an addition reaction with a suitable curing agent. The curing agent used will determine whether the epoxy cures at ambient or elevated temperatures and also influence physical properties such as toughness and flexibility. There are two basic types of epoxy resin, these being :

i) Bisphenol A - Diglycidyl Ether ii) Epoxy Phenol Novolac

Epoxy phenol novolac resins have the higher cross-link density of the two types and are used in high performance applications such as pre-pregs for the electrical industry and also in some high performance laminating applications.

Low viscosity, low molecular weight Bisphenol A epoxies are the ones most widely used in the composites industry. They are available as 2 pack systems which can be cured at room temperature using a suitable curing agent, the various types of which are as follows:-

B: Water

i) Amines (di - functional)

Cure is effected by two epoxy groups reacting with one primary amine and these are most widely used for 'standard' room temperature applications. As there are health implications with free amines, these systems are often supplied as amine adducts.

ii) Polyamides iii) Anhydrides

These curing agents react only with heat and need temperatures between 120°C and 140°C to be effective. They are used in high temperature applications such as filled, sanitary ware systems.

Epoxy resins are highly chemical and corrosion resistant. They have good physical properties and their low shrink characteristics mean they can be used where dimensional accuracy is of prime importance. Epoxies exhibit excellent adhesion to a wide variety of substrates including concrete, glass, wood, ceramics and many plastics.

This combination of properties makes epoxy resin suitable for use in many applications within the composites industry. These include adhesives, construction/repair, casting, laminating and flooring.

There are, however, health issues associated with resin sensitisation and cost can sometimes be a prohibiting factor.

Vinyl Ester Resins

Vinyl esters are thermoset resins which incorporate and build on the excellent physical properties of epoxy systems. They are used in similar applications to polyester resins, particularly where higher performance is required.

There are two basic types of vinyl ester resin, as follows :-

i) Bisphenol A - diglycidyl ether type (BADGE)

This type of vinyl ester is produced by reacting a BADGE system epoxy with methacrylic acid. The resultant resin is then diluted in styrene to produce a resin with a solids content of at least 50%.

BADGE vinyl esters are used mainly in high performance applications such as chemical tanks and pipes, though their use in the marine industry is becoming more widespread.

ii) Epoxy phenol novolac type (EPN)

This form of vinyl ester is a reaction product of EPN and methacrylic acid, diluted with styrene to a solids content of 30% to 36%.

EPN based vinyl esters have a higher cross - link density than BADGE systems which makes them suitable for more demanding applications, mainly in the chemical plant industry.

Vinyl ester resins have a molecular structure which allows them to react more completely than polyesters. This is due to the fact that in vinyl esters cross-linking is 'terminal' (ie. at the ends of the molecular chain) rather than throughout the chain as with unsaturated polyesters.

Because of this unique structure, vinyl ester resins can be used to produce tough laminates which are highly resistant to water and aggressive chemicals. They also exhibit a more rapid cure development which results in a reduction in print-through on the laminate surface. Optimum performance is only achieved, however, by post curing laminates at very high temperatures (at least 100° C). Laminates cured at room temperature will have similar physical properties to those made using a high performance polyester resin.

Phenolic Resins

Phenolic resins are polycondensates of phenols and aldehydes, or ketones and were first discovered in the late 19th century. The use of phenolic resins in the composites industry is relatively small, though growing and the most common type used is an aqueous resole phenol formaldehyde system, which cures in the presence of an acid catalyst. Phenolics are best suited to applications requiring high levels of fire retardancy, coupled with low smoke emission and low toxicity.

Due to the nature of the resin and catalyst systems, effective health and safety procedures and efficient ventilation/extraction systems are very important when using phenolic resins. Cross contamination of polyester resins should also be avoided in order to prevent inhibition of their cure.

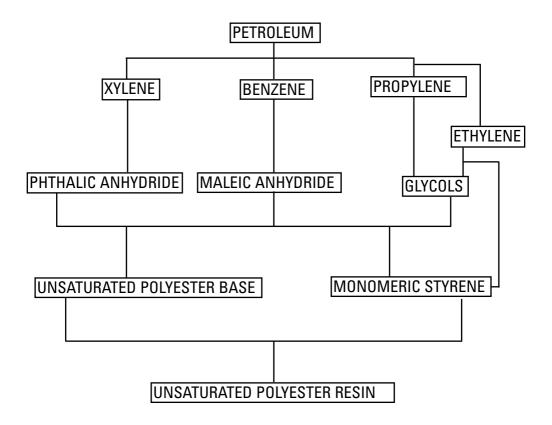
Hybrid Resins

Hybrid resins are produced by blending or reacting together resins of differing types, in order to impart the best properties of each to the new end product.

One such series of resins is the Crestomer* range which consists of urethane acrylate resins dissolved in styrene monomer. The urethane component is fully reacted into the molecular backbone. This contributes adhesive properties and flexibility without free isocyanate hazard, whilst the acrylate unsaturation and styrene monomer impart tough, hard, thermoset characteristics. The novel structure of these resins means they are compatible with and handle as well as, polyester resins and can be cured using conventional peroxide curing agents.

Urethane acrylates are used as base resins for formulated ranges of adhesives and high performance laminating systems, and as additions to unsaturated polyester resins, to enhance the performance of compounds and laminates.

Crestomer resins and adhesives exhibit excellent adhesion to many substrates, fibres and cured laminates. They are tough, resilient and flexible, with chemical resistance properties superior to those of a conventional flexible polyester. The filler tolerance of the materials is high and they are compatible with polyester pigments and thixotropic additives. Figure 1- Derivation of compounds used in the manufacture of a typical polyester resin.



Reinforcements

There are three main types of reinforcement used in the composites industry today; glass fibre, carbon fibre and polyaramid fibre.

Glass Fibre

The commercial availability of fine, consistent glass fibres, coupled with the development of low pressure polyester resins marked the birth of the fibre reinforced composites industry over fifty years ago.

Glass is an ideal reinforcing fibre for plastics. It is one of the strongest of materials (the ultimate tensile strength of a freshly drawn single filament of 9 - 15 microns diameter is about 3.5 GPa). Its constituents are readily available, it is non-combustible and also chemically resistant. Glass fibre is produced by drawing and rapidly cooling molten glass and is available in a variety of types and formats. Its final format will depend on how the drawn glass is further processed.

In the composites industry today, 'E' (Electrical) and 'C' (Chemical) are the predominant grades of glass used. The three most common 'E' glass formats are :

i) Uni-directional (all fibres in one direction) e.g. continuous rovings (UD)

ii) Bi-directional (fibres at 90° to each other) e.g. woven roving (WR)

iii) Random (fibres randomly distributed) e.g. chopped strand mat (CSM)

The predominant formats for 'C' glass are as surfacing tissues, which are widely used as chemical barriers and for aesthetic purposes.

Developments in glass fibre technology mean that glass reinforcements are now available in a wide variety of styles and formats, suited to diverse applications in many industrial sectors.

Carbon Fibre

Carbon fibre reinforcements have been available to the composites industry since the 1960's when high strength, high modulus fibres were first developed at the Royal Aircraft Establishment in Farnborough.

Carbon fibres are produced by carbonising a fibre precursor at a temperature between 1000°C and 3500°C. The most commonly used precursor is polyacrylonitrile (PAN). Fibres based on other, cheaper precursors are commercially available but their properties tend to be inferior to those of PAN based fibres. Properties such as density and elastic modulus are determined by the degree of carbonisation employed and carbon fibre reinforcements are now available to meet a wide range of strength and stiffness requirements.

Composites made using high modulus, uni-directional carbon fibre can exceed the modulus of steel. Bi-directional materials are more commonly used, however, to produce composite structures capable of meeting the stringent demands of high performance applications such as those in the aerospace industry.

Polyaramid Fibres

Polyaramid (Aromatic Ether Amide), fibres were discovered by DuPont in 1965. They are organic, manmade fibres, which have a unique blend of properties.

Polyaramid fibres are flame resistant, chemical and corrosion resistant and have excellent electrical

properties. Their light weight (density 1.4 - 1.45) combined with their strength and modulus characteristics result in specific strength and specific modulus properties, which are superior to all glass fibres and some carbon fibres.

There are two main grades of polyaramid fibre, one with an elastic modulus similar to that of glass fibre and one with an elastic modulus double that of glass fibre. The lower modulus material is used in ballistic applications, both as dry fibre and as a composite, whilst the higher modulus material is the one most widely used in the composites industry today.

Polyaramid fibres are used to produce composites which are light-weight and incredibly strong, with excellent impact properties. Some of them, however, exhibit low compression strength which should be taken into consideration where structures are likely to be subjected to flexure or compression loading.

Glass Combination Materials

Many glass fibre reinforcements are now available as combinations of styles and types, for instance woven roving stitched to a chopped glass deposit. These products have been developed to amalgamate the improved mechanical properties of a woven fabric with the ease and speed of application of a chopped mat or tissue.

Non-woven combination materials made from 'E' glass are also available. These products, which are crimp free, consist of layers of reinforcement held together by a light stitching. They are designed to maximise directional strength properties and are available in bi-axial, tri-axial or quadri-axial formats, some with a chopped glass backing for ease of use.

Hybrid Combination Materials

Reinforcements which contain more than one fibre type, are known as hybrids. The most common of these are polyaramid/glass and polyaramid/carbon combinations, though carbon/glass combinations are also available. The use of different fibres in one reinforcement results in a fabric which exhibits all the advantages of each constituent fibre, with none of the disadvantages. For instance, the use of a polyaramid/glass reinforcement will produce a composite with the impact resistance of polyaramid fibres and the compressive strength of glass fibres.

Speciality Materials

Developments in closed mould processes such as RTM have resulted in the introduction of specialised reinforcing materials which address the need for improved quality, speed and ease of production. These materials are available in various forms, from continuous filament mats to sophisticated pre-formed net-shapes.

The use of stitched products is increasing and a stitched mat specifically developed to optimise the speed and efficiency of closed mould processes is now available. It consists of chopped glass fibres stitched to each side of a non-woven synthetic core and allows a laminate thickness up to 6mm to be achieved per layer of material. The unique structure of this product means it is pre-formable when cold, easy to tailor and permits excellent resin flow through the mould.

Today's composites industry has access to an infinite variety of reinforcement types and styles. This enables specifiers and designers to create composite structures capable of meeting the most demanding of applications.

Cure Systems

In order to produce a moulding or laminate using a polyester resin, the resin must be cured. This is achieved either by the use of a catalyst and heating, or at room temperature by using a catalyst and an accelerator. Most Crystic resins are supplied pre-accelerated, incorporating an accelerator system designed to give the most suitable cure characteristics for the fabricator. These resins need only the addition of a catalyst to start the curing reaction at room temperature. Certain resins cannot be pre-accelerated, however, due to their cure characteristics and these require the addition of both an accelerator and a catalyst to initiate cure.

N.B. Catalysts and accelerators must never be mixed directly together since they can react with explosive violence.

Those catalyst and accelerator systems most commonly used in the composites industry are described in this section.

Catalysts

Organic peroxides are normally used as catalysts in the composites industry. Since these materials are unstable in their pure form, they are mixed with an inert compound before being supplied commercially. This process is known as phlegmatisation and is carried out during manufacture. Phlegmatisers are usually liquids (e.g. phthalates) or inert fillers (e.g. chalk) but other media are sometimes used.

The types of catalyst most commonly used, particularly in conjunction with polyester resins, are Methyl Ethyl Ketone Peroxide (MEKP), Cyclohexanone Peroxide (CHP), Acetyl Acetone Peroxide (AAP) and Benzoyl Peroxide (BPO).

MEKP Catalysts

Liquid dispersions of methyl ethyl ketone peroxide are most widely used in contact moulding applications (hand lay or spray). Various standard grades are available, differing only in their reactivity * and activity.

* 'Reactivity' and 'activity' must not be confused. Low reactivity catalysts simply extend geltime, whereas low activity catalysts can result in undercure if incorrectly employed.

CHP Catalysts

Cyclohexanone peroxide catalysts are available as powders, pastes and liquids and are used in contact moulding applications where a more gradual cure is required. In paste form, CHP catalyst can be made available in tubes.

AAP Catalyst

Acetyl acetone peroxide catalysts are used where fast cure times are required. The main use for AAP catalysts is in applications where fast mould turn-round is required, for example RTM and cold press moulding.

BPO Catalyst

Most benzoyl peroxide catalysts are supplied as powders, though paste versions and pourable suspensions are also available. Benzoyl peroxides are designed to cure at elevated temperatures (above 80° C), and they only cure at room temperature when used in conjunction with a tertiary amine accelerator.

TBPO and TBPB Catalysts

Tertiary butyl peroctoate and tertiary butyl perbenzoate are catalyst types commonly used in heat curing processes such as pultrusion and hot press moulding. They can be used singly, or in combination with each other, to adjust time/temperature curves to suit specific moulding requirements.

The catalysts described above are the standard materials most commonly used in the composites industry. As the composites industry has developed, cure technology has also advanced and catalysts are now available in a wide range of types, with properties tailored to suit the many applications and processes currently in use.

Accelerators

Many chemical compounds will act as accelerators for polyester resins, making it possible for catalysed resin to cure at room temperature. The most important of these are those based on cobalt soaps or aromatic tertiary amines.

Cobalt Accelerators

Cobalt accelerators consist of various concentrations of cobalt soap, usually dissolved in styrene. The standard strengths used are 0.4%, 1.0% and 6.0% though other concentrations are available.

Amine Accelerators

Amine accelerators are normally used in conjunction with Benzoyl Peroxide catalyst to achieve rapid cure at room temperature. They are usually supplied as solutions dissolved in styrene, phthalate or white spirit.

It is essential to choose the correct cure system and to use the correct level. If manufacturers' formulations are used under recommended conditions, the cured resin will achieve its maximum strength, durability, chemical resistance and stability, ensuring that the final moulding will attain optimum properties.

Fillers

When mineral fillers were first introduced to the composites industry it was as a means of reducing cost. At that time, excessively high loadings were used and this resulted in a serious deterioration in the mechanical strength and chemical resistance of mouldings produced.

Today, the effects of fillers are better understood and they are used to enhance and improve certain properties of a resin. Filled resins exhibit lower exotherm and shrinkage characteristics than unfilled systems, and they tend to be stiffer, though more brittle. The level of cost reduction achievable by the use of fillers is no longer a significant factor.

The range of fillers available is now wide and varied and some of those most commonly used are described overleaf.

Calcium Carbonate

Surface treated calcium carbonate fillers, particularly crystalline types, are widely used, especially where lower exotherm temperatures and lower shrinkage are desirable (e.g. casting or mould making applications).

Talc

Magnesitic talcs are used to increase 'bulk' and reduce exotherm temperature, usually in casting applications.

Metal Powders

Fine metal powders can be added to catalysed polyester resin to produce realistic metallic castings. Aluminium, brass, bronze and copper powders are all readily available.

Silica

Hydrophilic fumed silica is used to impart thixotropy to polyester resins. A high shear mixer is required to ensure adequate dispersion.

Microspheres

Hollow microspheres are available in glass and thermoplastic form. Glass microspheres are produced from 'E' glass, whilst polypropylene is the most common raw material for the thermoplastic spheres. Microspheres trap air in a spherical shell, so when incorporated into a resin mix, they increase volume, reduce weight and reduce shrinkage. Polyester putties, and cultured marble are two applications where microspheres are used to enhance the properties of the finished product.

Alumina trihydrate

Alumina trihydrate is a flame retardant filler used to improve the fire resistance of polyester resins. ATH is non-toxic, supresses smoke production and impedes burning.

Although its primary use is as a fire retardant, the translucent nature of ATH makes it ideal for use in casting and synthetic marble or onyx production. Specific grades are available for these applications.

Pigments

Most polyester gelcoats and resins can be supplied pre-pigmented, but pigment pastes are available to enable the fabricator to colour to his own requirements.

Crystic polyester pigment pastes are specially formulated for use in polyester gelcoats and resins and consist of fine pigment powders dispersed in a medium which cross-links into the base resin during curing. Recommended addition levels are between 8% and 10% for gelcoats and 4% to 5% for backing resins.

To ensure colour reproducibility, it is important that all sub-assemblies of multi-component mouldings are manufactured using the same mix of pigmented material.

Release agents are an integral part of the composite moulding process and are vital to the successful production of high quality FRP components.

The choice of release agent will be influenced by various factors such as mould size and complexity, moulding numbers, surface finish requirements, etc. Selecting the right one is very important in ensuring quality and consistency in the finished product.

The most common types of release agent are described in this section.

Polyvinyl Alcohol

Polyvinyl alcohol is available in concentrated form, or as a solution in water or solvent. It can be supplied coloured or colourless and applied by cloth, sponge or spray.

Polyvinyl alcohol-based release agents are normally used for small mouldings with a simple shape, or as a secondary release agent and are suitable for use on metal and FRP composite moulds.

Care should be taken when using polyvinyl alcohol-based release agent in vertical sections. Because it is low in viscosity it will drain down and accumulate in corners where it may take a long time to dry. If a moulding is laid up before any such areas are dry, it will almost certainly stick, causing damage to the mould.

Wax

Wax was first used as a release agent in the composites industry in the 1950's. Carnauba wax-based products are the most suitable for use with composite materials and these are widely employed, particularly in contact moulding applications.

Silicone modified products can be used but care has to be exercised as silicone can interfere with the release interface making separation difficult. Any silicone-based release agents should be thoroughly tested before use

Wax release agents are available in several forms but those most commonly used are pastes or liquids. Among the advantages of wax release agents are their ease of use, convenience and economy. Waxes are used mostly in low volume contact moulding applications, as the need for regular re-application can be time consuming. There is also the potential for problems, created by wax build-up and transfer.

Semi-permanent Systems

When applied to release agents, the term 'semi-permanent' usually refers to those products which function by depositing a micro-thin film on the surface of the mould. They usually consist of a polymeric resin in a carrier solvent and once applied to a mould surface the solvent evaporates leaving a resin interface.

Semi-permanent release agents allow multiple releases from moulds, making them ideal for high volume production processes such as resin transfer moulding (RTM). There is no build-up or transfer of release agent, so the need for cleaning of moulds and/or mouldings is reduced to a minimum. It is vital when using these unique release systems that the mould surface is perfectly clean to ensure good film formation and proper cure of the release coating.

Wax / Semi-permanent Hybrids

These materials normally consist of a wax amalgamated with a semi-permanent release agent. They combine the ease of use of a wax with the multi-release characteristics of a semi-permanent system.

As with semi-permanent release agents, wax/semi-permanent hybrids require mould surfaces to be perfectly clean before use if they are to be effective.

Release Film

Cellophane or polyester film is used as a release medium. It is not suitable for complex shapes but is an ideal system for use in the manufacture of composite sheeting or decorative flat panels.

Internal Release Agents

Internal release agents are used mainly in high volume, mechanised processes such as pultrusion, RTM and SMC / DMC hot press moulding. A suitable product is dissolved in the resin mix and during processing it migrates to the surface and forms a barrier between the resin and the mould.

Core Materials

Low density core materials are used in the manufacture of FRP composite components to increase stiffness without increasing weight. They can be employed in specific areas of a structure where extra stiffness is required (e.g. boat hull ribs), or throughout the area of a laminate to produce what is known as a 'sandwich panel'.

There are two categories of core material; structural and non-structural and some of the more commonly used types are described in this section.

Two-Component Polyurethane Foam

The two components of this material are mixed 1:1 by volume to produce a rigid polyurethane foam. The foam expands rapidly to approximately 25 times its original volume and is used in buoyancy and general gap-filling applications.

Polyurethane Foam Sheet

Sheets of rigid, closed cell polyurethane foam can be used as a core in sandwich construction, or for making formers. It is normally used in non-structural applications, though structural grades are available for use in fast production processes.

Grooved polyurethane foam sheet is also available. This is used as a non-structural core in applications where conformity to curved surfaces is required.

PVC Foam

Closed cell, linear and cross-linked PVC foams are used as structural cores in marine, transport, building and many other applications. They are tough, rigid materials and their high strength and stiffness to weight ratio makes them ideal for the production of light weight sandwich panels.

They are available as plain sheets, perforated sheets and also as scrim cloths (squares of foam bonded to a glassfibre scrim).

Polyetherimide Foam

Polyetherimide foams are used where resistance to fire is important. They do not burn, produce negligible amounts of toxic gas and smoke and maintain their properties at temperatures up to 180°C.

Styrene Acrylonitrile Foam

This material combines high strength and stiffness with low water absorption and low creep values, making it ideal for use in offshore buoyancy applications.

Balsa Wood

End-grain balsa wood has been used as a core material for many years. Classified as a hardwood, balsa has a very high strength to weight ratio and can be used in structural or non-structural applications.

As a non-synthetic (ie. natural) product, balsa can be inconsistent in density and unless it is kiln dried, its moisture content can cause problems. It is also generally more dense than most foam core materials.

Honeycomb Cores

Honeycomb cores are manufactured from a variety of plastic and metal materials and are used to produce composite structures with extremely high strength to weight ratios.

Two common types of honeycomb core are aluminium and phenolic coated, polyaramid fibre papers which are both used extensively in the production of components for the aerospace industry.

Non-Woven Core Materials

Non-woven cores are chemically bonded materials impregnated with micro-spheres. These materials produce laminates with high stiffness to weight ratios and high impact and shear resistance.

They are easy to use, with excellent drapability and conformability and are compatible with most unsaturated polyester resin systems.

A secondary advantage of these materials is the prevention of print-through, which is achieved due to improved resin distribution and lack of shrinkage in the core material.

Adhesives

The development of adhesive materials specifically designed for applications in the composites industry has resulted in a marked increase in their use. Adhesives are now available to fulfil most requirements, from relatively simple bonding functions through to technically demanding structural applications.

There are four main adhesive technologies employed in today's composites industry. All of these are described in this section, together with Scott Bader's unique Crestomer range of adhesives.

Polyester Resins

Crystic polyester resins are used to produce bonding pastes which are viscous, filled compounds designed for the assembly and bonding of FRP mouldings. They are used in mainly non-structural or semi-structural applications such as internal frames, ribs, hull to deck assemblies and car components, to give moderately high shear strengths without the need for mechanical fixings.

Epoxy Resins

Epoxy resins are used to produce structural adhesives suitable for many applications. Epoxy based adhesives will bond a wide range of substrates including composites, metals, ceramics and rubber. They can be formulated to impart heat and chemical resistance and to exhibit gap filling and other required properties. Adhesives based on epoxy resins are capable of achieving very high shear strengths and are used extensively in structural bonding applications in the aircraft industry.

Acrylic (Methacrylate) Resins

Adhesives based on methacrylates are tough, resilient materials with high shear, peel and impact strengths. They can be formulated to bond to many substrates and to operate over an extensive temperature range. Very short cure times are achievable with this class of adhesive, thus allowing fast turn-round times.

Polyurethane Resins

Most polyurethane based adhesives are moisture curing materials. They are extremely flexible and adhere to a wide variety of substrates. A combination of high peel strength and moderate shear strength makes these adhesives suitable for use in varied applications from sealing to structural bonding.

Crestomer (Urethane Acrylate) Resins

The adhesive properties of Crestomer materials are due to the novel structure of the base urethane acrylate resin. The urethane component is fully reacted into the molecular backbone, contributing adhesive properties and flexibility without isocyanate hazard. The acrylate unsaturation and styrene monomer impart tough, hard thermoset characteristics. Crestomer adhesives therefore exhibit excellent adhesion to substrates such as foam and balsa core materials, cured composites and metals.

The Crestomer range is tailored for specialist adhesive and construction requirements such as structural and semi-structural bonding, filleting, core bonding and gap filling.

Recent developments in Crestomer technology mean this unique adhesive system is now available in cartridge form, with various cure options, thus extending even further its areas of application.

Mould Making Materials and Ancillary Products

Many mould making methods are employed within the composites industry, depending on the nature of the finished product, and each method requires its own supplementary materials. The diverse nature

of products, processes and manufacturing methods creates a need for an extensive range of ancillary materials.

This section deals with a range of ancillary items available to maximise the manufacture and quality of composite products.

Flexible Mould Making Materials

These compounds are widely used in the decorative casting industry and there are three main types available:

- i) Latex Rubber:- This is commonly used, in dipping form, to produce small resin castings such as chess pieces.
- ii) Vinyl-based Synthetic Rubber:- Vinyl-based synthetic rubbers are available in solid form and are melted in a purpose designed melting pot. The grade used depends on the requirements of the finished product, with a durable grade for limited production runs and a flexible grade for complex originals. Moulds can be cut up and melted down for re-use.
- iii) Cold Cure Silicone Rubber:- This material is used to produce durable, high definition moulds with excellent reproduction of fine detail. It is a two part system comprising a base and a catalyst and is ideal for longer production runs. Thixotropic additives are available to convert the material from a pourable liquid to a 'butter-on' form, if required.

Plaster and Clay Materials

High strength mould plasters are used to produce rigid moulds for limited production runs. It is important that plaster moulds are sealed and have suitable release agents applied, before use.

High strength clays, which can be oven hardened, are commonly used to produce detailed formers, whilst general purpose modelling clays are used for temporary filling and filleting applications.

Wax is also widely used, in sheet and fillet form, in mould production.

Composite Mould Making Materials

Contact moulding is the most commonly used method of composite production and the moulds used in this process are normally themselves produced from composite materials. A separate section has, therefore, been devoted to the subject of materials and processes for composite mould manufacture (see Mould Making Section).

Polishing Compounds and Associated Products

The appearance of a fibre reinforced composite product can be greatly enhanced by polishing the surface after release from the mould.

Polishing compounds and their associated products designed specifically for use with composites are now widely available. These include compounds for hand and machine application, polishing cloths and bonnets and finishing glazes.

PROCESSES

Open Mould Processes The development, in the 1950's, of resins which cured in the presence of air led to the introduction of contact moulding processes, which still dominate many areas of the composites industry.

Contact moulding is a particularly adaptable method of manufacturing composite components of all shapes, sizes and complexity for relatively little capital investment. Only one mould is needed and this can be male or female, depending on which face of the moulding needs to be smooth.

There are three main techniques used in contact moulding, these being hand lay-up, spray lay-up and roller saturator. Whichever technique is employed to produce a contact moulded part, the construction of the mould plays a vital role in determining the quality of the finished component. For this reason, a complete section is devoted to materials and procedures for mould making, later in this handbook.

Gelcoating

The durability of a composite moulding is very dependent on the quality of its exposed surface. Protection of the surface is achieved by providing a resin rich layer, which normally takes the form of a gelcoat. Special care must be taken in the formulation and application of the gelcoat, as it is a very important part of the laminate and is also the most vulnerable part.

Thorough mixing of the gelcoat is extremely important, particularly when adding catalyst, as inadequate catalyst dispersion will result in uneven cure of the gelcoat, which may impair its physical properties. Poor mixing of pigment will result in surface imperfections which will detract from the appearance of the moulding, so it is recommended that pre-pigmented gelcoats are used wherever possible. The use of low shear mechanical stirrers helps to minimise any potential mixing problems.

Gelcoat can be applied by brush or spray, though developments in gelcoat technology and spray equipment have combined to markedly increase the use of spray application methods. Whichever application method is chosen, it is important to use a gelcoat from the Crystic range, specially formulated with the correct rheology for that method.

The various types of spray equipment available are described later in this section.

For optimum performance, it is important to control the gelcoat thickness to 0.4mm - 0.5mm and as a guide, $450\text{g}-600\text{g/m}^2$ of gelcoat mixture will give the required thickness. If the gelcoat is too thin it may not cure fully and the pattern of the reinforcing fibre may show through from the backing laminate. Thin gelcoats are also prone to solvent attack from the resin used in the backing laminate and this can result in gelcoat wrinkling. If the gelcoat is too thick, it may crack or craze and will be more sensitive to impact damage, particularly from the reverse side of the laminate. A gelcoat of uneven thickness will cure at different rates over its surface. This causes stresses to be set up in the resin which may lead to crazing or, in the case of pigmented gelcoats, a patchy appearance and watermarking.

Full, even cure is vital if a gelcoat is to achieve optimum performance, so it is important that cure conditions and systems are controlled. Workshop and material temperatures should be maintained at a minimum of 18°C and a medium reactivity MEKP catalyst should always be used, at a 2% addition level. In deep moulds the cure of a gelcoat can be inhibited by the accumulation of evaporated styrene fumes. Extraction of these fumes is, therefore, necessary to ensure even gelation of the gelcoat.

Once the gelcoat has cured sufficiently, the next step in the contact moulding process is to apply the backing laminate. A simple test to assess the state of cure of the gelcoat is to gently touch the surface with a clean finger. If the surface feels slightly tacky, but the finger remains clean, then the gelcoat is ready for laminating, which should commence within five hours.

Laminating

Hand Lay-Up

Chopped strand glass fibre mat is the reinforcement most commonly used in contact moulding, though the

use of woven and various combination materials has grown considerably over the years. The preparation of reinforcement 'packs', specifically tailored to the mould being used, saves time and reduces wastage.

The amount of resin required for a laminate can be calculated by weighing the reinforcement to be used. For chopped strand mat the resin to glass ratio should be between 2.3:1 and 1.8:1 (30% to 35% glass content). Resin to glass ratios of approximately 1 to 1 (50% glass content) are normal for woven roving, whilst those achievable with combination reinforcements will vary depending on the construction of the particular fabric used.

Once the gelcoat has cured sufficiently, a liberal coat of resin is applied as evenly as possible. The first layer of glass is then pressed firmly into place and consolidated using a brush or roller. This action will enable the resin to impregnate the glass mat and dissolve the binder which holds the fibres together. The reinforcement will then conform readily to the contours of the mould. Once the first layer of mat is fully impregnated, further resin can be added, if necessary, before applying subsequent layers of reinforcement. It is important that the first layer is as free of air bubbles as possible, as any air trapped immediately behind the gelcoat could lead to blistering, should the moulding be exposed to heat or water during its working life.

Impregnation of the reinforcement can be carried out using a brush, or a mohair or polyester roller. If a brush is used, it should be worked with a stippling action, as any sideways brushing motion will displace the fibres and destroy their random nature. The use of rollers is advantageous when working on large moulds and they are available with long or short pile. Long pile rollers pick up more resin than short pile ones, but care needs to be taken to accurately control resin to glass ratios. Consolidation of the laminate is more effective if carried out using a roller and several types have been developed for the purpose. Metal paddle, disc or fin rollers are available, and of these, thin fin types have proved particularly effective in removing air bubbles trapped in the resin.

Subsequent layers of resin and reinforcement are applied until the required thickness has been achieved, ensuring that each layer is thoroughly impregnated and properly consolidated. It is recommended that no more than four layers of resin and reinforcement are applied at any one time, to prevent the build up of excessive exotherm. High exotherm temperatures can lead to gelcoat cracking, pre-release, distortion or scorching of the laminate. Where thick laminates are required, each series of four layers should be allowed to exotherm, then cool, before subsequent layers are applied, though lengthy delays should be avoided \unless a resin with a long green stage is used. 'Green stage' is the term used to describe the period between gelation and cure of the resin, during which time it is in a soft, rubbery state. In this condition, the laminate can be easily trimmed to the dimensions of the mould and trim edges can be built into the mould to facilitate this operation.

Should a moulding need to be strengthened, this can be achieved by incorporating reinforcing ribs into the laminate. The stage at which the ribs are put into position will depend on the shape, thickness and end use of the moulding, though as a general guide, it is best to locate them immediately before the last layer of reinforcement is applied. The rib formers should be covered with reinforcing mat and thoroughly impregnated with resin. The final layer of reinforcement can then be applied over the whole area of the moulding to give a uniform appearance to the back surface.

Metal inserts are sometimes necessary, as locating or fixing points, etc. and these can be put into place during the laminating operation. If an insert is likely to be subjected to a heavy load, the thickness of the moulding should be tapered away from the insert, in order to spread the load. Inserts should be positioned as near to the middle of the laminate as possible and the contact area between laminate and insert should be as large as practicable.

Today's composites manufacturers benefit from the availability of a wide range of metal fasteners and inserts specially developed for the industry. The development of adhesive systems in the Crestomer range means that metal inserts can now be bonded directly into laminates, thus reducing production times.

Where pieces of reinforcement require joining to cover the surface of a mould, butt or lap joints can be used. Butt joints should be made with care so that no space is left between the two edges and lap joints should not overlap by more than 25mm (unless required for stiffening). Joins in chopped strand mat can be made less conspicuous by spreading the excess mat on either side by rotating a brush in small circles along the line of the join.

The back surface of a moulding can be rather coarse in appearance, particularly if chopped strand mat is the reinforcement used. This can be improved in one of two ways; either by incorporating a surface tissue as the final layer of the laminate to give a smoother, resin rich surface, or by coating the surface, once it has cured, with a formulated flowcoat such as that in the Crystic range. The use of a flowcoat gives the added advantage that it can be pigmented if required.

Spray Lay-up

This technique involves the use of a spray gun for the simultaneous deposition of chopped glass and catalysed resin onto the surface of a mould.

A chopper unit attached to the spray gun chops glass rovings into specified lengths (usually between 20mm and 50mm), and the chopped strands are then directed towards a stream of catalysed resin as it exits the spray gun.

Those resins in the Crystic range which are designed for spray application are generally low in viscosity, so they rapidly wet out the chopped strands. This ensures they are more easily atomised into the desired spray pattern. The rapid wet -out achieved by spray deposition allows faster and easier consolidation than would be achieved with hand lay methods, but thorough rolling of the laminate is still necessary to ensure complete air removal. The efficiency of the catalyst dispersion in the resin can also be checked at this stage. If using resins which incorporate a colour change mechanism on catalyst addition, or catalysts which contain coloured dyes, the uniformity of catalyst dispersion can be easily monitored.

Many commercial spraying systems are now available but due to their higher output and convenience, pumped systems are more common than the older pressure pot equipment, particularly for the production of larger mouldings.

Spray Equipment

Pumped Systems

There are three principal pumped systems, as follows:-

1) Airless Atomisation

Compressed air is used to operate pumps which transfer resin or gelcoat from their original containers to the spray gun. Catalyst is then introduced either within the gun (internal mix) or immediately after it leaves the gun (external mix). The gelcoat or resin is forced through a small spray tip at high pressure in order to atomise the material and produce a fan. Compressed air is not used directly to atomise the material, hence the term 'airless atomisation'. The pressure on the gelcoat can vary between 57 bar (800 psi) and 214 bar (3000 psi), depending on the type of equipment used. Catalyst is metered into the resin stream by either a catalyst pump linked to the resin pump, or from a catalyst pressure tank.

2) Air Assisted Airless

This system is a variant of the airless system which combines conventional air atomisation and airless techniques to allow the use of lower atomising pressures (typically 28.5 bar to 57 bar or 400 psi to 800 psi). The gelcoat is pumped at relatively low pressure and atomising air is introduced through a modified spray tip in order to refine the spray pattern and eliminate 'fingering', etc. The lower pump pressures used in this system can reduce output compared to a standard airless system, but porosity in the applied gelcoat film tends to be lower and styrene emissions are reduced.

3) HVLP Systems

High volume, low pressure spray guns have been used for some time in the paint industry but are relatively new for gelcoat application.

These systems utilise high volumes of air at low pressure (typically 0.7 bar or 10 psi or less), in order to atomise gelcoats with minimal styrene emission.

Other types of spray equipment commonly used are gravity fed, siphon and pressure pot systems.

Gravity Fed Systems

In this method, a container holding catalysed, accelerated material is attached to an industrial spray gun fitted with a suitable nozzle. The container is held above the gun and flows into it under gravity. Because of their thixotropic nature, gelcoats applied using this method tend to feature a coarse, 'orange peel' effect on their back surface and output is rather slow. The equipment requires little cleaning and maintenance, however, so can be useful for applying gelcoat to small moulds, particularly if frequent colour changes are required.

Siphon Guns

The use of spray guns which operate by the siphon system is normally restricted to the application of gelcoat in minor repair work. This is due to the fact that output is rather slow because of the thixotropic nature of the material.

Pressure Pot Systems

In this system, material is held in a pressure vessel. It is forced to the spray gun at low pressure (typically 2.1 bar to 3.5 bar or 30 psi to 50 psi), where it is atomised by a separate air stream. Atomisation can take place within the gun, but it is more commonly external to the gun as the material exits the spray tip.

Atomising pressures generally range from 3.5 bar to 5.0 bar (50 psi to 70 psi).

Pressure pot systems produce smoother, more uniform films at a faster rate than gravity fed or siphon systems, but are significantly slower and less convenient than pumped systems, particularly where large moulds are involved. For example, where the catalyst is added to the gelcoat in the pressure pot (hot pot systems), production runs are limited by the working life of the material, as it is essential to spray the mould and clean the equipment within this time. However, these systems are relatively simple to operate and maintain and can be useful for small to medium sized moulds where regular colour changes are required.

Airless, air assisted airless and HVLP catalyst injection systems employing internal or external catalyst mixing mean that spray equipment is available to meet the diverse needs of individual users. Units capable of multiple colour gelcoat spraying are also readily available.

Although spraying does not solve all the problems inherent in hand lay contact moulding, it is now widely used throughout the composites industry. In the hands of a skilled operator most types of spray equipment will significantly increase output compared with hand application.

Roller/Saturator Lay-up

Roller/Saturator equipment is designed to saturate glass reinforcements such as chopped strand mat, cloth or woven rovings with activated resin. The resin is held in a container and pumped as required to a roller head.

It is relatively easy to control the resin to glass ratio of a laminate using this method and significantly less styrene is released into the atmosphere during laminating operations.

The use of a roller/saturator is ideal for large mouldings such as building panels and large radius boat hulls, etc.

The moulding methods previously described in this section are all cold curing processes so the laminates produced can take several hours to mature. It is possible to accelerate the curing process by applying a moderate amount of heat to the moulding, taking care to raise the temperature slowly to avoid styrene evaporation or blistering.

For gelcoats, the temperature should be raised to 30-35°C measured on the mould and, once the gelcoat has gelled, it may be necessary to allow the mould to cool before proceeding with the backing laminate. Once laminating is complete, the temperature can be raised again, but it should not exceed 35°C before gelation. After gelation, the temperature can be increased gradually to 60°C and maintained for about one hour. The moulding should then be allowed to cool back to ambient temperature before removal from the mould.

Mould Release

Provided the mould release agent has been correctly applied, release should be a fairly simple operation. The edge of the moulding should be eased away from the mould using plastic wedges designed for this purpose and then a direct pull will usually effect release of the moulding. With more difficult shapes the use of compressed air between the mould and the moulding will assist release and compressed air points can be built into the mould during its construction. Boat hulls and mouldings of similar shape can be separated by running water slowly between the moulding and the mould, provided a water soluble release agent has been used. On large, thick moulds, it may be necessary to strike a few careful blows with a rubber mallet on the outside surface of the mould. This should, however be a last resort as it can result in cracking of the mould surface.

If a split mould has been used, screw or hydraulic jacks can be employed to part the separate pieces. The

mould flanges must be heavily reinforced and several jacks used, to ensure that even force is applied over the length of the flanges.

Post Curing

Contact moulded laminates can take several weeks to fully mature at ambient temperature but this period can be reduced by post curing at elevated temperatures. Best results are obtained by allowing the moulding to stabilise for 24 hours at ambient temperature and then post curing for either 3 hours at 80°C, 8 hours at 60°C, 12 hours at 50°C or 16 hours at 40°C. These times and temperatures are for general guidance only and where mouldings are to be used for water or chemical containment, different conditions may apply.

Trimming and Finishing

Production time can be saved if mouldings are trimmed while the resin is still at the 'green' stage. This operation is best carried out using a sharp trimming knife which is held at right angles to the laminate, though scissors can be used. If suitably reinforced, the edge of the mould can be used as a trimming guide, but care should be taken not to distort or delaminate the moulding at this stage.

Fully cured composite laminates are difficult to cut or machine using conventional steel tools. Water jet and laser jet cutters are now readily available for large scale machining of composites, but for smaller operations a full range of portable diamond or carbide tipped cutters and drills is available. Many of these operate by means of compressed air, making them safe for use in the workshop. The health and safety aspects of handling and machining composite materials are dealt with in a separate section later in this handbook.

Once all trimming operations are complete, any release agent should be removed from the surface of the moulding prior to buffing and polishing. Where a moulding is to be painted, wax release agents should be avoided as they are difficult to remove without the use of wet or dry rubbing paper. Most paint systems can be used with composites but, for stoving finishes, it is recommended that the moulding is post cured at 80°C before applying the paint. Special primers, designed to achieve excellent adhesion to gelcoated surfaces, are available and their use is recommended for durability. Sandable gelcoats in the Crystic range have also been developed specifically to enhance the paintability of composite mouldings.

Closed Mould Processes

For many years, contact moulding has been the predominant method of manufacturing composite components. Whilst it is a particularly adaptable process, legislative and commercial pressures are making it less cost effective as a production method.

Many closed mould processes, which address the environmental and quality/consistency issues inherent in open mould methods, are now available to composite moulders. These cover a wide range of production and technical needs, from relatively low volume, low capital cost through to highly automated, large volume, high investment processes.

Vacuum Infusion : VI

This process can be introduced to a moulding shop with minimum investment. Existing open moulds can be used with little or no modification, and the process is adaptable to large or small components.

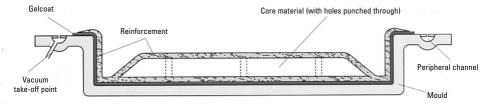
In the VI process, dry reinforcements are encapsulated between a rigid, airtight mould and a flexible membrane (vacuum film or 'bag') which is sealed around the edge of the mould. This forms a cavity which is then placed under vacuum to compact the reinforcement.

Catalysed resin is introduced into the cavity and the vacuum pulls it through the reinforcement. Once the component is fully infused, it is allowed to cure, after which the bag and the component are removed from the mould.

Resins for use in the VI process need to be low in viscosity and may also require controlled exotherm properties, for larger sections or thicker components.

There are several variants of the VI process, the most significant of which is probably the SCRIMP^{*} system developed by William Seeman in the United States of America.

Vacuum Infusion



tooling.

VacFlo is operated by applying a gelcoat to one or both mould faces as required, placing the reinforcements and any core materials in the lower tool and closing the mould. A vacuum (approx. 1 bar or 14 psi) is pulled between the double seal around the perimeter of the mould, effectively clamping the two halves together. A second vacuum (approx. 0.5 bar or 7 psi) is then pulled in the cavity of the tool using a centrally placed vacuum port.

Catalysed resin is introduced via an injection port at the edge of the part. The resin may be drawn in using vacuum only, or by using a combination of vacuum and injection under pressure. As the resin enters the cavity it flows around the perimeter and then into the centre of the tool. Once the mould is full, injection is stopped and the mould is held under vacuum until the resin has gelled. When cured, the part is demoulded.

The VacFlo system will work with VI or RTM resins, so the moulder can select materials from the Crystic range to best suit his conditions.

Resin Transfer Moulding : RTM

Developments in materials, machine and tooling technologies have enabled the RTM process to become highly efficient for both small and large components and short or long production runs.

The basic RTM process involves pre-loading a mould cavity with dry, continuous reinforcement, closing the cavity and injecting a catalysed resin. Once the resin has wet-out the reinforcement and has cured



sufficiently, the cavity is opened and the part removed.

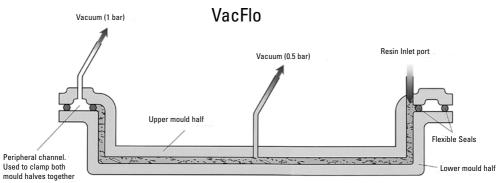
RTM tools can be manufactured from composites or, for maximum durability, from metals. The tools may operate at room temperature or incorporate a heating system for optimum production.

The RTM process is now widely accepted in the composites industry as an effective method of manufacturing parts ranging from aerospace applications through to land transport, marine and building and construction. For RTM it is vital that the gel and cure characteristics of a resin can be tailored to suit particular mould cycle times.

Cold/Warm Press Moulding

This technique involves the use of a pair of matched tools which are mounted in a press. The tools are often constructed from composites and are either used at room temperature, or modest temperatures up to 60° C.

To operate the process, a gelcoat is applied to the required mould face (normally the female half).



Once the gelcoat is sufficiently cured, the reinforcement is put in place. Finally, the required amount of catalysed resin is poured into the mould and the tools are closed.

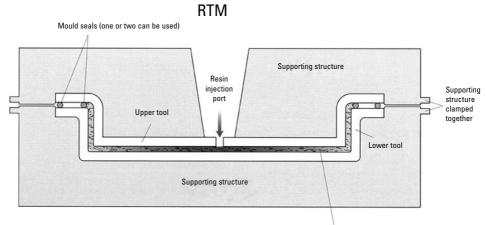
As the mould halves are compressed together, the resin is forced to flow through the cavity and wet out the reinforcement. By using a pinch-off around the perimeter of the tool, it is possible to allow air to vent while still creating sufficient back pressure to ensure the resin fills all areas of the cavity.

It is possible to use vacuum to draw the moulds together and act as the press, in which case no external

press is necessary and the moulds can be light weight and semi-rigid.

Resin requirements for press moulding are similar to those for RTM, though in certain circumstances the geometry of the part requires a more thixotropic product. Resins, reinforcements and associated products in the Crystic range are specifically designed to enable moulders to optimise whichever closed mould process is chosen.

Although closed mould techniques generally require more capital investment than contact moulding methods, they have many advantages. Quality can be more closely controlled and closer dimensional





tolerances achieved, leading to mechanical properties which are more consistent and easier to accurately predict. One of the greatest benefits of closed mould systems, however, is their impact on the environment, as styrene emissions during moulding can be virtually eliminated by using these processes.

Hot Mould Processes

Hot press moulding techniques are used for high volume production of composite components. The principle of the process is that reinforcement and a controlled quantity of catalysed resin are enclosed and cured between heated, polished, matched metal moulds. A hydraulic press is used to bring the moulds together under pressure at temperatures between 100°C and 170°C. Cycle times, which are dependent on temperature, moulding complexity and weight, are generally between 2 and 4 minutes but can be as low as 30 seconds.

The same equipment can be used to produce components by 'wet moulding' or by the use of moulding compounds or 'pre-pregs'.

Wet Moulding

Dry reinforcement is placed into the mould and catalysed resin poured onto it. The resin is catalysed using a curing agent which is activated by the heat of the mould but is stable at ambient temperature. The hydraulic pressure created by the closure of the mould forces the resin through the reinforcement and into the pinch off area, thus ensuring total wet out of the reinforcing fibre. Pressure is released once cure has taken place and the component is then removed from the mould.

Where the wet moulding technique is used, it is possible to pre-form glass reinforcement before putting it into the press. Chopped rovings are sucked or blown onto a fine mesh shaped to the right contours. When the desired thickness of reinforcement is achieved, the pre-form is sprayed with binder to hold the strands together, then oven heated for 2 - 3 minutes at a temperature of 150°C. The pre-form is then ready for the

press.

Moulding Compounds

Today's composites industry employs hot press techniques mainly to produce components from polyester moulding compounds supplied to the moulder in ready to use form.

Dough Moulding Compound (DMC)

This is a dough like mixture normally based on polyester resin and 'E' glass fibres. General purpose DMC's use calcium carbonate as the filler, though other fillers may be used to obtain specific properties required in the moulding. The reinforcing fibre length is normally between 3mm and 12mm and the fibre content of a finished moulding would be between 15% and 20%.

Bulk Moulding Compound (BMC)

BMC is similar in appearance to DMC but is formulated to produce mouldings of improved quality and finish. Isophthalic resins are used as these exhibit better hot strength and stability and low profile additives may be incorporated to improve surface finish.

N.B. When moulding compounds were first developed, the main difference between BMC and DMC was that BMC contained a chemical thickener (e.g. MgO), whereas DMC was unthickened. Today, most moulding compounds are unthickened and the two terms are interchangeable. The term DMC is used extensively in the UK and USA, with BMC being used exclusively in most of Europe.

Sheet Moulding Compound (SMC)

SMC consists of 'E' glass reinforcement impregnated with catalysed polyester resin containing various fillers. It is supplied in sheet form sandwiched between two polyethylene or polyamide films.

To mould SMC, sufficient pieces of the sheet material are cut to between 40% and 80% of the surface area of the mould in order to make up the desired weight of the finished moulding. The pieces are stripped of their protective film and placed in the mould where the application of heat and pressure will cause the compound to flow throughout the tool cavity. This homogeneous flow occurs even when the mould has deep draw areas or sectional changes and gives a constant resin : glass ratio throughout the moulding. This allows complex parts including those with ribs, bosses and changes in section to be manufactured.

SMC produces mouldings with excellent dimensional stability, high mechanical properties, good chemical resistance and electrical insulation. Minimal shrink grades of SMC are available, and these can be used to achieve a superior surface finish for post painting. SMC is therefore suitable for the production of automotive body parts, electrical housings, chemical trays etc.

Low Pressure Moulding Compound (Crystic Impreg)

Crystic Impreg is similar to SMC but uses a novel, patented technology to physically thicken the compound during manufacture, rather than the conventional method of chemical thickening using a reactive filler.

Crystic Impreg can be moulded using much lower pressures than SMC. For optimum results, the moulding process requires a pressure of 5 - 25 bar and a temperature of between110°C and 150°C, which will give a cycle time of 2 - 10 minutes depending on part size and complexity.

Crystic Impreg LPMC can be moulded with great consistency immediately after manufacture, using relatively low capital cost presses and utilising tools produced from a wide range of materials. Its unique chemical make-up allows many different grades to be prepared for use in various applications including the automotive industry. This means that features such as shrink control, fire resistance, improved toughness and water resistance can be incorporated, thus tailoring the material to suit end user requirements.

Continuous Processes

Continuous processes are used to produce composite components such as sheeting and pipes, which are suited to long, uninterrupted production runs. Several continuous processes are described in this section.

Pultrusion

The pultrusion process is used to produce composites of uniform cross - section with exceptional longitudinal strength and rigidity. The process was first used in the 1950's to produce simple items such as rod stock. Since then, developments in process and material technology mean that highly complex profiles of considerable dimensions can now be manufactured using this method.

Expressed simply, the process involves drawing reinforcements, impregnated with activated resin through a forming guide, which pre-shapes the material. Using continuous rovings, which are usually the predominant reinforcement present, the material is pulled through a heated die, which activates the catalyst, thus curing the resin. The cured profile then passes a flying saw attachment and is automatically cut to the required length.

The reinforcement is wetted out either by the use of a resin bath, or by resin injection at the front of the die. The resin bath system is still the most common, though resin injection is gaining in popularity and is more environmentally friendly as it drastically reduces styrene emissions.

The curing system used in the pultrusion process usually consists of a combination of peroxides. A highly reactive peroxide, known as a 'kicker', is used for initial cure, in combination with medium or low reactivity peroxides to achieve a more gradual through cure. This dual system ensures that profiles achieve optimal cure, with low residual styrene contents.

The cured profile is pulled through the die using either reciprocating pullers or a continuous caterpillar track system. The reinforcement most commonly used in the pultrusion process is glass, though carbon and polyaramid fibres can also be used successfully. Resin systems for pultrusion include polyesters, vinyl esters, epoxies and methacrylated resins, with polyesters being the most common.

Pultrusion resins in the Crystic range are designed to achieve the balance of properties necessary to optimise the process.

Filament Winding

The filament winding process is based on a simple basic principle. It consists of impregnating reinforcing fibres with activated resin, then winding them onto a rotating mandrel. Successive layers of reinforcement are built up on the mandrel until the required thickness is achieved. The reinforcement can be wound longitudinally, circumferentially, helically, or in a combination of two or more of these. The properties required from the finished article will often determine the angle of wind.

The mandrel, though normally of steel, may be made from a variety of materials, and pressurised, flexible mandrels are often utilised in the manufacture of certain types of cylindrical vessels. In the case of composite components using PVC, polypropylene, etc. as a lining material, the prefabricated liner takes the place of the mandrel.

Continuous rovings are generally used in this process though other forms of reinforcement such as woven tapes can be incorporated. Glass, carbon and polyaramid fibres can all be used successfully. Glass and thermoplastic veils are often included where resin rich corrosion barriers are required.

Polyester, vinyl ester and epoxy resins are all suitable for use in the filament winding process, resin choice being dependent on the requirements of a specific application.

Filament winding is an ideal process for the fabrication of cylindrical composite products and is widely used for the production of large tanks, process vessels, ducting and pipes capable of meeting stringent performance requirements.

Pullwinding

Pullwinding is a process which combines pultrusion with filament winding and is used to produce thin wall, hollow composite profiles which exhibit high strength properties.

Reinforcements, impregnated with activated resin, are wound onto a mandrel, which is then pulled through a heated die. As in conventional filament winding, the reinforcement, which is normally a roving, can be wound in one or more of several directions.

Those resins and reinforcements suitable for filament winding and pultrusion can also be used in pullwinding.

Centrifugal Moulding

This process is used to mould tubes, pipes and cylinders with a maximum diameter of 5 metres. Chopped roving or glass mat is laid inside a hollow mandrel and impregnated with activated, normally polyester, resin. The mandrel is then heated and rotated until the resin cures. This process creates centrifugal force, which acts to consolidate the laminate. Un-reinforced cast resin sheet can also be produced using the centrifugal moulding method.

Resins from the Crystic range, which were developed for use in the filament winding process, are also suitable for centrifugal moulding.

Machine Made Sheeting

Most of the composite corrugated sheeting manufactured today is produced using machines. There are several patented machine processes, all of which are similar in principle.

A continuous length of release film, usually polyester, travels along a moving conveyor and glass fibre is fed onto it. Activated polyester resin is then metered onto the glass and a further layer of release film added to complete a glass/resin 'sandwich'.

The sandwich passes under a series of rollers which consolidate the laminate, control its thickness and expel any air. The laminate is then passed into a heated forming area on the machine and corrugated by means of dies or rollers. Heat can be applied in this area by means of an enclosed oven, or by a series of heat lamps suspended above the surface. Once the laminate is formed and cured, it is trimmed to the

correct width and then cut to the desired length, usually by means of an automatic saw.

'E' glass is always used in the machine manufacture of transparent composite sheeting, either in mat form or as randomly deposited chopped rovings. This is because the refractive index of 'E' glass can be matched by specialised polyester resins to produce sheeting of high clarity.

Some of today's automated sheeting manufacture utilises ultra violet (UV) light to cure the laminate, so Crystic resins with specially designed curing mechanisms have been developed to meet this need.

Resins in the Crystic range are available to enable the machine production of composite sheeting with a range of properties including low fire hazard, good weathering and high clarity.

APPLICATIONS

Un-reinforced Polyester Resin

This handbook is mostly concerned with the application of polyester resins in the fibre reinforced composites industry. However, polyester resins are also widely used in un-reinforced applications, some of which are described in this section.

Body Filler

Polyester based compounds are used extensively for the cosmetic repair of vehicle bodies, to rectify damaged composite mouldings and for many other repair/refurbishment applications where rapid completion is important. These compounds are also ideally suited to the production of formulated wood fillers and plaster fillers.

Crystic Stopper is a formulated material which consists of a liquid resin base and a filler powder. When these are mixed together in the recommended proportions they form a paste, which cures at room temperature. The paste is easy to apply with good trowelling properties and rapid cure characteristics. It provides a hard, rigid filling, which can be mechanically sanded without clogging. This material is ideally suited to the 'do-it-yourself' market.

Crystic resins for formulators to compound into body fillers are designed to achieve the ideal combination of storage stability with optimum curing properties. The properties required from the formulated compound are achieved by varying the combination and type of filler used. This can be a complex process, as purity, softness, particle size and size distribution of the filler will all affect the performance of

the final system.

Flexibility in the cured compound is important to ensure good adhesion and to impart optimum finishing and sanding characteristics. The level of flexibility is largely determined by the resin constituent of the compound and can be tailored by incorporating one or more resins of different flexibility into the formulation. Advances in resin formulation and production techniques have enabled body filler technology to progress to meet the demands of this technically oriented application.

Button Casting

Polyester resins have, for many years, been used to manufacture buttons. There are three main methods of manufacture depending on the type of button being produced.

Pearl buttons are generally manufactured from resin pigmented with natural or synthetic pearl essence. The pigmented resin is cast into sheets, normally by centrifugal casting methods. The buttons are then either blanked from the sheets before they are fully cured, or trepanned from totally cured sheets and finally machined and polished.

Plain buttons can be manufactured from rod stock. Resin is cast into tubes made from suitable materials such as polyurethane. The buttons are cut from the resulting rod stock at the required thickness, machined and polished on the cut surfaces. Various effects (e.g. tortoiseshell) can be achieved by the use of two or more coloured pigments added to the resin.

Large, decorative or textured buttons are usually moulded individually in multi-cavity silicone rubber moulds attached to a moving belt. Resin is poured into the moulds, the belt is vibrated to remove air and then passes through an oven to heat cure the resin. Little or no machining is required with this method of manufacture.

Embedding and Potting

Glass clear polyester resins can be used for embedding objects to produce paperweights and other decorative items, or for preserving medical and botanical specimens. These resins can also be used very effectively in the production of costume jewellery.

The excellent dielectric properties and curing characteristics of certain Crystic resins makes them ideal for encapsulating electronic components. These range from single capacitors to complete miniaturised circuits.

Decorative Casting

Polyester resins are widely used in the manufacture of decorative articles such as statuettes, figurines, models and replicas, etc.

Expressed simply, the casting process involves mixing an inert filler powder into a resin, pouring the mix into a mould and leaving it to cure.

Self releasing, flexible mould compounds are most commonly used for casting purposes. The three main types of moulding compound are latex rubber, hot melt vinyl rubber and cold cure silicone rubber.

The choice of filler powder for decorative casting depends to a large extent on the final finish required.

If the casting is to be pigmented or post painted, then the filler is needed only to bulk out the resin and calcium carbonate or talc can be used. Alumina trihydrate will produce castings with a semi - translucent finish reminiscent of marble, whilst marble flour itself can also be used to achieve this affect.

Powdered metals used as fillers result in castings with a realistic metal finish. Bronze, copper, aluminium and brass powders are all available and they can also be mixed together to create different metallic effects. For instance, mixing aluminium and a small quantity of brass will produce a good simulation of old, tarnished silver. Metallic castings must be buffed and polished after removal from the mould in order to produce the realistic metal sheen.

General purpose and specialised polyester resins in the Crystic range have been developed to cater for all aspects of the decorative casting industry.

Polyurethane resins are also used for decorative casting, as they produce strong, durable castings with very high definition and excellent reproduction of fine detail. They are easy to mix and measure and finished castings can be painted using enamel, acrylic, and oil paints. Polyurethanes are widely used in the commercial manufacture of high quality model kits.

Flooring

Specially formulated Crystic polyester resins have, for many years, been used to produce seamless industrial and decorative flooring systems. When properly laid and cured on suitably prepared substrates they have outstanding resistance to a wide range of chemical environments. Polyester floors have an attractive, aesthetic finish, which is durable, hygienic and easy to clean and maintain.

Polyester flooring systems generally consist of three component resins, these being a primer, a base coat and a topcoat or glaze. The primer is formulated to provide adhesion to suitably prepared substrates, the base coat is a clear resin which can be pigmented and filled and the topcoat is a clear resin used to seal the flooring system and provide the aesthetic finish.

Polyester Concrete

Resin based concrete can be an attractive, lighter weight alternative to cement based concrete pre-castings and natural slate. Developments in resin technology coupled with extensive field experience, has enabled a range of previously cement based concrete structures to be pre-cast with resin aggregate compositions. With suitable resin, filler, aggregate and pigments a range of pre-castings, including claddings, tiles and simulated slates can be manufactured with attractive, durable finishes.

Resin concrete formulations for pre-castings are prepared by mixing an activated polyester resin with appropriate fillers and aggregates to suit specific applications. For example, a synthetic slate can be produced from polyester resins filled with slate powder and other fillers. Artificial stone can be produced either by reconstituting natural ground stone or by using standard fillers with suitable pigments. Polyester systems, such as Crystic resins, offer greater versatility than other polymers because their cure characteristics can be adjusted without seriously affecting the properties of the finished product. Finished pre-castings, properly cured, are durable when exposed to natural weathering and their properties can be optimised to maximise resistance to particular environments. Other benefits of polyester pre-castings include improved impact and mechanical properties, fine mould reproduction, fast setting and rapid property development.

Polyester Marble and Onyx

Simulated marble and onyx, produced using polyester resins, are used to manufacture basins, vanity units, profiled panels, etc. Cladding panels for walls, stairs and columns are also attractively produced in these materials.

Simulated marble is manufactured by mixing an activated polyester resin with a suitable grade of powdered filler such as calcium carbonate (typically 75% by weight). Small additions e.g. 2% to 5% by weight, of light weight glass bubbles are sometimes added to improve the hot and cold water cycle resistance of the material, thereby reducing the calcium carbonate content.

Simulated onyx is usually lighter in colour and more translucent than simulated marble. Colour is more critical and formulations are normally based on alumina trihydrate (typically 67% by weight) or glazed frits (typically 75% by weight).

When a base colour is required, pigment pastes are mixed into the resin. The variegated effect is achieved by partially mixing in pigments which are dispersed in an incompatible medium, and using artistic judgement to develop and reproduce the desired marble or onyx effect. The application of a clear gelcoat to the mould before pouring in the filled resin mix gives an added in-depth lustre to the finished article.

Solid Surfaces

Fibre reinforced unsaturated polyester resins have been used in building applications for many years. Recent developments in granite-effect surfaces have created new potential for their use in decorative finishes for industrial and domestic applications.

Solid surface castings are manufactured using high quality, Iso-NPG polyester resins such as those in the Crystic range, containing coloured, unsaturated or saturated polyester based chips and an alumina trihydrate filler.

Resin based solid surface materials can be mixed and moulded using vacuum, so do not require a gelcoat to achieve a good surface finish. This means that the surface can be re-polished, when necessary, to restore the original 'showroom' gloss.

Solid surface castings are easy to machine and can be routed to enable different colours to be inlaid, thus allowing an infinite range of decorative finishes.

Solid surface castings are tough and durable and exhibit excellent water and heat resistance. These properties mean they are ideally suited for kitchen surfaces, sanitaryware and washrooms. The excellent weather and chemical resistant qualities of the base resin used in solid surface technology creates the potential for its use in external cladding applications.

Rock Anchors

Rock anchors are used in mining, civil engineering and building/construction applications, to provide 'strong points' for bolts/rebars.

Resins for rock anchors need to balance very long storage stability with the apparently conflicting requirement of very rapid cure. A range of geltimes can be obtained, varying from a few seconds to several hours, depending on the particular cure system used.

The most important mechanical property required from a rock anchor is compression strength, though good adhesion is also important.

Fillers for use in rock anchors are crucial in terms of their 'pull-out' properties and storage stability. Those commonly used vary from large silica pieces, which literally float in the resin, to finely ground limestone. The type of filler used will depend on the application. Filler purity is important, as this can affect the properties of the anchor. It is advisable to avoid fillers with high contents of transition metals such as iron and cobalt, as these can adversely affect storage stability.

Cartridge or 'sausage' packaging is commonly used for rock anchors in the civil engineering and mining industries. The resin is sealed in a styrene resistant plastic such as nylon, and a glass tube or plastic film containing catalyst is incorporated within the package. The action of fixing the bolt or rebar into place mixes the catalyst, which is dispensed at a set ratio (commonly 10:1).

Rock anchor resins from the Crystic range are tailored to meet the demanding requirements of this application.

Chemical Containment

Composites have been used for many years to manufacture products for resistance to, and the safe containment of, a wide range of chemicals.

Chemical resistant FRP composites generally consist of high tensile strength glass fibre protected by a chemically resistant unsaturated polyester resin. Figures 2 and 3 give examples of the specific tensile properties achievable with glass fibre reinforced polyester laminates, in comparison with steel and aluminium. The ease of use and versatility of FRP facilitates the cost-effective manufacture of a wide range of components, using a variety of manufacturing processes. Typical material and fabrication costs are shown in Figure 4.

Composite structures offer many benefits over alternative materials, in chemical containment applications. They are light weight so simplify handling and installation. Being self coloured, they need no re-painting and are easily cleaned using a high pressure hose. If necessary, composite structures can be modified in-situ, with minimum interruption of normal operations.

The ability of a resin to resist a particular chemical environment is normally classified in terms of its 'Maximum Operating Temperature'. In the case of chemical resistant Crystic resin based laminates, these

temperatures have been determined from a number of sources including case histories, laboratory tests and practical experience.

Provided that the composite structure is manufactured to high standards and fully post cured, many years' satisfactory service is achievable. Chemical tanks should always be designed in accordance with the requirements of British Standard 4994:1987, which uses the 'K' factor of safety approach. (A new European Standard, pr EN 13121, is currently being developed and will eventually replace BS 4994:1987).

In acid environments, GRP can suffer premature degradation due to stress corrosion cracking of the glass fibre reinforcement. It is therefore important to ensure that the structural laminate is adequately protected by a substantial barrier layer. This can consist of a thermoplastic liner, or several millimetres thickness of GRP made using 'C' glass or synthetic surface tissue and a highly resin rich 'E' glass laminate. The recommended barrier layer should be backed with an appropriate resin, reinforced with an acid resistant glass such as 'ECR' (Extra Chemical Resistant) glass.

Polyester resins from the Crystic range are used to manufacture a wide range of products and components for the safe containment of most materials from acids to alkalis, fuels to foodstuffs and water to wine.

Figure 2 - Specific Tensile Strength - Steel, Aluminium and GFRP

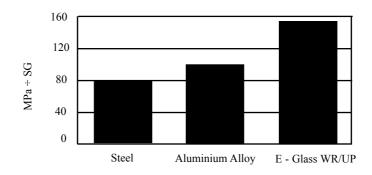


Figure 3 - Specific Tensile Modulus - Steel, Aluminium and GFRP

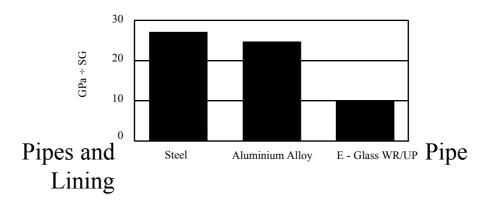
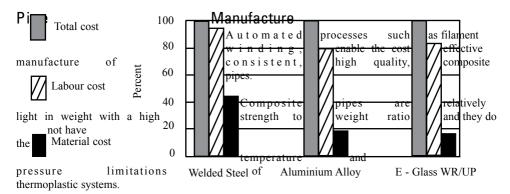


Figure 4 - Comparative material and fabrication costs for component manufacture



A resin rich barrier layer provides resistance to chemical attack and erosion and the angle of helix, or wind, will determine strength characteristics.

Polyester, vinyl ester and epoxy resins are all suitable for use in pipe manufacture, but resin choice will often depend on the specified requirements of a particular application. The Crystic range contains systems formulated to resist a wide range of chemical environments and operating conditions.

Pipe Lining

Repairing or replacing damaged pipes can be expensive and difficult, particularly where the pipe concerned is in an inaccessible situation. The "cured in place" structural lining process offers a cost effective solution to this problem.

A tube liner consisting of a polyester felt impregnated with catalysed, high quality resin, is tailor made to the dimensions of the damaged pipe and is inverted using water pressure. Once inverted, the catalysed resin in the liner is activated and cured. Curing is normally achieved using hot water, though ambient curing systems are also used in certain cases.

When cured, the liner ends are removed and lateral connection re-opened using robotic cutter units. The completed liner is then surveyed and the line re-commissioned.

This system offers many benefits, including:-

- * A cost effective alternative to pipe or conduit replacement
- * No disruption to the ground or fabric surrounding the pipe, resulting in minimal disturbance to the client
- * Joint free and leak proof, with fast installation
- * Structural properties adaptable by choice of lining thickness and resin selection
- * Chemical resistance tailored to suit both municipal and industrial applications

Resins from the Crystic range are used extensively in this demanding application.

Marine

Composites have been used in the marine industry since the early 1950's. Today, composite vessels feature in virtually every area of the marine market, from small leisure craft to large yachts, fishing boats, lifeboats and passenger ferries.

There are many benefits to be gained by using composite materials in boat building. Composites are strong, durable and readily moulded into complex shapes of almost unlimited dimensions, thus allowing freedom of engineering design. The appearance of composite vessels is aesthetically pleasing and they are weather and corrosion resistant, resulting in reduced maintenance compared with other materials. Today, high performance polyester, vinyl ester or epoxy resins are combined with high strength fibres such as glass, carbon and polyaramid to manufacture craft with outstanding physical properties. Specialised resins, which impart toughness to conventional polyesters, have enabled the production of high performance craft which can withstand extreme impact and flexural loading without cracking.

Developments in other products such as core materials, now allow the manufacture of light weight, stiff, high performance craft that are extremely resistant to the marine environment. This is achieved by a process known as Sandwich Construction where a low density core is sandwiched between FRP skins. This process is further described in the Properties section of this handbook.

High performance pigmented gelcoats and in-mould coatings ensure that all the components which comprise a completed boat exhibit a high quality outer surface which requires minimal finishing.

Advances in structural adhesive technology have resulted in the replacement of mechanical fasteners with tough, shock absorbing adhesives, in many marine applications.

Matched Performance Marine Systems

The Crystic Matched Performance system was developed as the result of extensive research into osmotic blistering in composite boat hulls.

The Matched Performance concept involves chemically matching fully formulated isophthalic gelcoats and laminating systems to create synergy within the composite structure.

When used as part of a quality manufacturing approach, Matched Performance systems offer many benefits beyond the elimination of osmotic blistering. Strength, rigidity and long term performance are all improved, thus allowing the full potential of composite structures in the marine market to be realised.

Today's marine industry is highly sophisticated and uses composite materials throughout the boat building process. The Crystic and Crestomer ranges contain resin and adhesive systems designed to fulfil the needs of the industry today and in the future.

Land Transport

Composites are the ideal materials for coach building and all types of specialist vehicle bodywork construction. They are equally suited to large scale body units, limited production runs, one-off prototypes, and vehicles for high performance or specialist applications.

Because composite materials are easily moulded into complex shapes, they can be used to produce any component from a single panel, through multi-panel sections to complete units of any size.

Composites are light weight with excellent strength to weight ratios and are easily designed to meet specific criteria such as impact resistance, insulation properties, fire resistance, etc.

The strength, durability and weather resistance of composites mean they require minimal maintenance and any accidental damage is easily repaired.

Composite vehicle bodies are aesthetically pleasing, with high quality gelcoats and in-mould coatings producing self-coloured units or readily paintable components.

Gelcoats and resins from the Crystic range are used to produce a wide range of vehicles, from high performance sports cars to ambulances, lorry cabs, caravans and train cabs.

Developments in materials and processes ensure that composite materials will remain at the forefront of transport technology well into the future.

Building and Construction

Composites are extremely versatile and have been used in many areas of the building and construction industry for more than thirty years. Modules and cladding are the two most popular ways of using composites in building. Modular composite construction is an extension of long established prefabrication techniques, which utilise to the full the light weight nature of composite mouldings. As they are manufactured in a mould, it is relatively easy to produce large numbers of identical modules in various geometric designs.

The ability to be formed into complex shapes, to be textured and to simulate natural materials such as wood, slate, etc., are among the reasons for the successful use of composites as external cladding materials.

The light weight and excellent strength to weight ratios of composites enable designers to meet specific criteria such as impact resistance, insulation properties and fire resistance.

Composite modules and cladding panels are aesthetically pleasing and their strength, durability and weather resistance means they require minimal maintenance compared to many conventional building materials.

High performance gelcoats and resins ensure that all components which comprise the exterior of a composite structure exhibit a high quality surface which requires minimal finishing.

Resins and gelcoats in the Crystic range have a proven track record of over thirty years in the building and construction industry. The use of these materials offers architects, civil engineers and other specialists exciting opportunities to provide unique benefits and attractive solutions to building design today and in the future.

PROPERTIES

General Concepts

Composites have many advantages over conventional materials. The ability to design and build large structures conceived as a whole, rather than an assembly of parts which have to be joined together means, for instance, that boat hulls can be built with fuel tanks as an integral part of the moulding. Outstandingly stiff structures can be made by the use of appropriate geometric shapes to produce light weight space frame structures with both rigidity and strength. This type of design has been used to great effect in the construction of composite buildings and bridges.

It is possible to vary laminate thickness in local areas of a composite moulding and to increase the strength characteristics at any point in any direction simply by making intelligent use of the reinforcing fibre.

If the full benefits of composite materials are to be realised, then adequate design is essential. This means taking into consideration not only the properties of the intended laminate but also the method of fabrication which is to be used.

It is important to approach each design challenge by thinking of composites as structural materials in their

own right, rather than just as replacements for traditional materials.

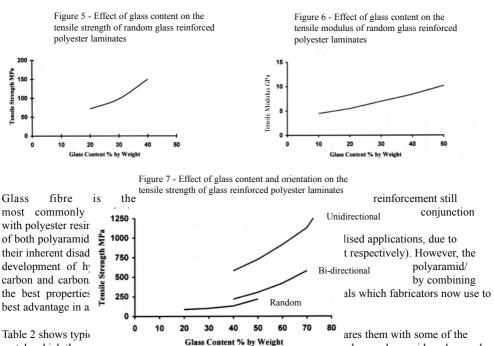
The remainder of this section deals with the various properties of composite materials. It is not intended to be used as design data, but to give basic information on the properties of composite materials.

Mechanical Properties

The mechanical properties of a composite will be influenced by the mechanical properties of its constituent parts. It is therefore useful to examine the basic properties of cast, un-reinforced resins with those of various reinforcing fibres, before appraising composites as engineering materials. Table 1 compares the typical properties of various resins and reinforcing fibres used in composite manufacture.

As well as the obvious effects of resin and fibre type, the mechanical properties of a composite will be influenced greatly by the resin to fibre ratio achieved in the laminate and by the orientation of the fibres. Figures 5, 6 and 7 show the affects of differing resin to glass ratios and orientation on the tensile properties of glass reinforced polyester resins.

Table 1 - Comparative Properties of Cast Un-reinforced Resins and Fibres



metals which they (

hybrid reinforced composites, using a medium reactivity isophthalic from the Crystic range as the resin matrix.

The fatigue and creep properties of glass fibre reinforced polyester composites will be specific to the loading criteria applied and the material tested. For instance, glass cloth laminates will give a superior performance in creep to random glass mat laminates. Although the fatigue characteristics of FRP composites compare favourably with many metals, it should be borne in mind that metals are isotropic materials, so predicting fatigue and creep is relatively easy. This is not the case with composites, which are anisotropic.

There are several differences between glass fibre reinforced polyester and metal. For instance, ductility is relatively poor in GRP which has an elongation at break of about 2% compared with about 40% for steel.

glass, polyaramid, carbon and

Table 2 - Typical properties of glass reinforced composites compared with steel and aluminium alloy.

	CSM (PB)	WR	Satin Weave	UD - CSM	WR - CSM	Mild	Aluminium
			Cloth	Combination	Combination	Steel	Alloy
Resin	Ortho - Polyester	Iso - Polyester	Iso - Polyester	Iso - Polyester	Iso - Polyester	-	•
Post Cure	16h 40°C	16h 40°C	28 days RT	16h 60°C	16h 40°C	-	-
R : G Ratio (by weight)	2.33 : 1	1:1	0.81:1	1.3 : 1	1.16:1	• B.S.15	
Stress Direction	-	0°/ 90°	0°/ 90°	0° 90°	0°/ 90°	* HE15WP	
Specific Gravity	1.46	1.7	1.7			7.8	2.8
Tensile Strength (MPa)	110	220	260	300 25	180	450	300
Tensile Modulus (GPa)	8	14	17	16 7	12	207	70
Charpy Impact Strength (kJ / m ²)	75					50	25
Specific Tensile Strength (MPa)	75		-	-	-	31	154
Specific Tensile Modulus (GPa)	5.5					27	26

Table 3 - Comparative properties of glass, polyaramid and carbon reinforced polyester laminates.

	Unit	Glass* (WR)	Polyaramid*	Carbon*	Glass/ Polyaramid*	Glass/ Carbon*	Polyaramid/ Carbon*
FibreFraction by Weight	%	56.2	40.5	45.3	25.7	27.2	21.13
Laminate Thickness	mm	3.23	4.08	4.13	4.05	3.42	4.47
Tensile Strength	MPa	333	345	410	403	352	364
Tensile Modulus	GPa	15.2	20.9	36.1	19.0	29.1	29.5
Flexural Strength	MPa	389	301	378	349*	324×	298"
Flexural Modulus	GPa	13.6	14.6	28.4	15.0*	24.6×	23.2 ^e
Lap Shear Strength	MPa	6.7	7.1	9.6	9.0	6.5	8.0

*Tested in Warp Direction × Glass in Compression • Polyaramid in Compression ε Carbon in Compression

On the other hand, the deformation of unidirectional GRP is elastic almost to the point of failure, whereas the elastic limit for steel is about 0.2%.

From an engineering design standpoint, lack of stiffness has always been the most distinctive feature of FRP composites when compared with metal. Although developments in reinforcement technology have enabled up to four fold increases in their moduli for little or no increase in thickness, glass reinforced composites still do not approach the stiffness characteristics of steel, as can be seen from Tables 3 and 4. There are various ways of increasing the stiffness of FRP composites, the simplest of which is to increase thickness. However, a three fold increase in thickness would be required for a random glass mat laminate to achieve a similar stiffness to steel. This would increase cost and, more importantly, weight, thus negating one of the principal reasons for choosing composites in the first place.

In practice, one or more of the following methods has been commonly used to increase the stiffness of composite mouldings:-

- 1. Localised increases in thickness. Progressive local edge thickening or flanging along the edge of a panel will greatly improve its stiffness.
- 2. Laminating integral ribs into the reverse side of the laminate. This method is often used on large boat hulls.
- 3. Introducing compound curvature or local corrugations. If corrugations are introduced as part of the

general styling of a moulding, they need not be unsightly. This method can be further elaborated by a folded plate construction where the overall geometry of the structure gives the necessary rigidity. Using this system stiff structures can be produced from very thin sheets, making it an important method for producing large structures.

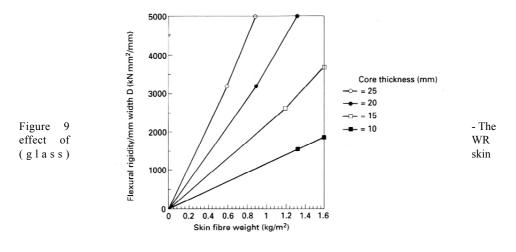
4. Sandwich construction. Since stiffness is a function of thickness, it is possible to form a rigid, yet light weight sandwich by bonding two outer skins of FRP to a low density core material. The core material can be balsa wood, foam, honeycomb or synthetic fibre, and information on the various core materials used is contained in the 'Materials' section of this handbook.

In sandwich construction, the FRP skins resist bending stresses and deflections, whilst the core resists shear stresses and deflections, withstands local crushing loads and prevents buckling of the FRP skins in compression. Sandwich construction can be used for localised stiffening (e.g. boat hull ribs) or to produce complete light weight rigid structures and the type of core material used will depend on the nature of the application.

For high performance applications such as those in the aerospace industry, honeycomb cores are used extensively. These may be manufactured from aluminium, or from fibre papers such as phenolic coated polyaramids. In the case of non-structural or less demanding structural applications, balsa, foam or non-woven core materials are more commonly used.

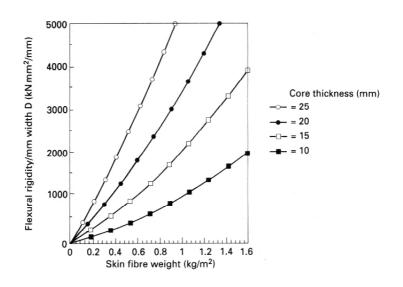
Figures 8 and 9 illustrate the rigidity of sandwich laminates in bending, using various CSM and WR skin and core thicknesses. The theory of FRP sandwich construction is complex and more detailed explanations can be found in various publications such as Polymer Engineering Composites (Applied Science) and the BPF Handbook of Polymer Composites for Engineers (Woodhead). (See Appendix 1)

Figure 8 - The effect of CSM skin construction (at R:F = 2.3:1) and core thickness on flexural rigidity for balanced double skinned sandwich laminates



construction (at R:F 1:1) and core thickness on flexural balanced double skinned sandwich laminates

rigidity for



The

temperature at which a composite structure is to operate may have an effect on its mechanical properties, and in some applications the retention of properties at elevated temperatures will be an important parameter.

At low temperatures properties often improve compared with room temperature values, but as temperature increases and approaches the Heat Deflection Temperature of the resin matrix, there will be a dramatic reduction in properties.

Table 4 illustrates the percentage retention of room temperature properties for a fully cured isophthalic polyester/chopped strand mat laminate.

Property	Temperature (°C)					
	- 68	- 40	23	70	130	225
Tensile Strength	98	98	100	104	56	33
Tensile Modulus	105	94	100	65	34	·
Elongation	100	129	100	143	143	-

Table 4 - Percentage retention of tensile properties at various temperatures. CSM reinforced isophthalic

polyester resin with an HDT of 116°C

The uniqueness of composites lies in the fact that the material of construction and the end product are produced simultaneously, so the material itself can be designed to have the particular properties required by the designer. This increases the versatility of composite design and also necessitates accurate property prediction.

Measured laminate properties can be used as a guide to the most suitable laminate for a given application, and theoretical models now exist which enable the designer to calculate or predict the properties of virtually any laminate construction.

In terms of tensile strength and modulus, figures are available for the minimum properties of reinforced laminate plies, or layers. These are based on the ultimate unit tensile strength, and extensibility or unit modulus, both of which are quoted as N/mm width per kg/m^2 of reinforcement. The simple law of mixtures also works well for tensile modulus predictions, but is not so successful in predicting tensile strength due to the difficulties in the choice of effective ultimate fibre strength. In some cases, an empirical approach to strength prediction is probably the preferred option. Table 5 shows U.U.T.S values for various glass and polyaramid reinforcements, and Figures 10 and 11 show the predicted effect of fibre type and content on tensile strength and tensile modulus using data from Table 5.

Table 5 - Minimum properties of reinforced	laminate plies (layers)
--	-------------------------

Reinforcement	Ultimate unit tensile strength (N/mm width per kg/m ² of reinforcement)	Extensibility (unit modulus - N/mm width per kg/m ² of reinforcement)
Glass		
CSM	200	14 000
WR (0°, 90°) (balanced)	250	16 000
UD roving	430	25 000
UD (continuous filament - 0°)	500	28 000
UD - 90°	0	8 400
Polyaramid		
Woven (0°, 90°) (balanced)	600	35 000
UD(0°)	1200	70 000

Figure 10 - Predicted effect of fibre type and content on tensile strength using property data from Table 5

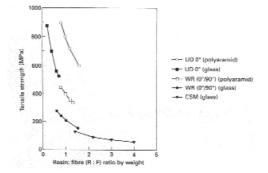
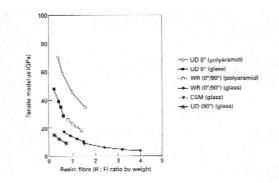


Figure 11 - Predicted effect of fibre type and content on tensile modulus using property data from Table 5



Detailed information regarding property predictioncan be found in publications such as BPF Handbook of Polymer Composites for Engineers (Woodhead) and Composites-Design Manual (James Quinn

Associates). (See Appendix 1)

Thermal and Electrical Properties

The thermal properties of a composite will depend to a great extent on the resin matrix, as well as the type of fibre reinforcement used, the alignment of the fibres and the volume fibre fraction.

The temperature resistance of a polyester resin is normally expressed in terms of either heat deflection temperature (HDT) or glass transition temperature (Tg).

To measure HDT, a rectangular bar of cast resin is immersed in oil and subjected to a bending load of 1.80 MPa. The temperature of the oil is raised at 2°C per minute, and the temperature at which the resin bar deflects by 0.25mm is quoted as the HDT of the resin.

The measurement of Tg does not involve any loading of the sample. It is a measurement of the temperature at which a cast resin softens sufficiently to change from a glass like state to a rubber like state, and one way of measuring it is by means of a differential scanning calorimeter (DSC). A small sample of cast resin is

placed into the machine, and the temperature reduced to 0° C. The sample is then heated at a constant rate and the softening point of the resin recorded.

The coefficient of thermal expansion (CTE) of fibre reinforced composites will depend greatly on the type and alignment of fibres used, as well as on the Tg of the resin matrix. The CTE of a laminate reinforced with uni-directional fibres will exhibit different CTE values in the 0° and 90° direction, whilst random glass reinforced composites demonstrate a constant CTE in all directions. The CTE of uni-directional carbon or polyaramid reinforcements will be negative in the 0° plane, and positive in the 90° plane. It is therefore possible to design composites to meet almost any required thermal expansion characteristics.

The CTE of a random glass reinforced composite is close enough to the CTE of steel, to enable the lining of mild steel tanks with GRP. This is only the case, however, for operating temperatures below 60°C as the CTE of the two materials differs considerably above this temperature. Table 6 compares the thermal properties of various materials.

Material	Thermal Conductivity (W / m °C)	Coefficient of Thermal Expansion (x10 ⁶ / °C)	Maximum Working Temperature (°C)
UD GFRP 0°	0.3	9	250
90°	-	14	-
UD Carbon** 0°	34	- 0.5	
90°	0.8	25	-
UD Polyaramid** 0°	1.7	- 4	
90°	0.14	57	
WR GFRP	0.24	15	-
Random GFRP	0.2	30	175
Mild Steel	50	12	400
Aluminium Alloy	200	23	200

** Epoxy resin matrix

Table 6 - Comparative thermal properties

** Epoxy resin matrix

GFRP and polyaramid composites offer good electrical insulation, whilst carbon composites conduct electricity.

The Crystic range contains polyester resins specifically developed for high performance thermal and electrical applications such as those in the aerospace and electrical industries. Table 7 shows typical electrical properties for un-reinforced polyester resins.

 Table 7 - Typical thermal & clectrical properties of cast

 polyester resin

Property	Unit	Value
Specific Heat	kJ/kgJ	2.3
Thermal Conductivity	W/mK	0.2
Coefficient of Thermal Expansion	x10 ⁻⁶ / °C	100
Permittivity at 50 Hz		3.7
Permittivity at 5 MHz		3.2
Power Factor at 50Hz		0.008
Power Factor at 5 MHz		0.019
Voltage Breakdown 0.2mm sample	kV / mm	22
Volume Resistivity	TΩm	1
Coefficient of Static Friction		0.27

Table 7 - Typical thermal & electrical properties of cast polyester resin

Fire Properties

Introduction

Fire performance is an important criterion in many of the applications in which composites are used. The building / construction, aerospace and land transport industries generally require high levels of fire resistance from many of the materials used for both structural and non-structural components.

Unsaturated polyester resins are organic, being composed of carbon, hydrogen and oxygen atoms, and, like all organic compounds, they will burn. However, by altering their structure and / or by the use of additives or fillers, it is possible to modify their burning behaviour. This enables the production of composite structures which present a reduced hazard under fire conditions.

The behaviour of FRP composites in a fire will depend on a number of factors, such as :-

- Ease of ignition
- Surface spread of flame
- Fuel contribution
- Fire penetration
- Smoke obscuration
- Toxic gas emission

When low fire hazard resins were first introduced for use in composite production, ease of combustion and flame spread were seen to be the main concerns. Today, the dangers of smoke production and toxic gas emissions during burning are well understood and resins which minimise these dangers are now available.

Fire Tests

Many tests for fire behaviour exist and most countries still have their own standards. Industries such as aerospace and rail transport have also developed fire tests and specifications to meet their special requirements and some of these have been incorporated into National Standards.

Common European and International Standards of fire performance are gradually being introduced, and one such standard is the Euroclassification of Reaction to Fire Performance of Construction Products and Related Test Methods which has been developed as part of the EU 'Construction Industry Directive'. This standard, which is expected to be finalised and implemented as BS EN 13501-1, should have come into effect during 2001, and will eventually replace British Standard 476 as the fire performance standard for the UK construction industry.

This section describes the more common methods used to assess the fire performance of composite materials. Most of the tests described require specialised equipment and have to be carried out by independent test centres, though there are simple laboratory tests which can indicate how a system is likely to perform in a fire situation.

Simple Horizontal Burning Tests

There are several laboratory scale tests of this type, including those specified in BS 2782 and BS 3532. Usually, a strip of material 150mm x 12.5mm is clamped horizontally and a test flame is applied to one end. The material under test may be an un - reinforced resin specimen or a laminate ; the test flame can be from a gas or an alcohol burner and the results can be expressed as a burning time, a burning rate or the

Limiting Oxygen Index Test

This laboratory test measures the level of oxygen required to sustain combustion. Samples are exposed to a small flame in an oxygen/nitrogen atmosphere. The level of oxygen is adjusted until the sample continues to burn for a specified period, and this level becomes the oxygen index. The higher the LOI, the more difficult it will be for a flame to spread.

British Standard 476 - Fire Tests on Building Materials and Structures

British Standard 476 has been the mainstay of fire performance testing in the UK for many years. It comprises several parts, not all of which relate to FRP composites. Some of the parts which are used in assessing composite fire behaviour are described below.

Part 3: 1958 - External Fire Exposure Roof Test

This test was updated in 1975, but the 1958 version is still widely used as it is referred to in many building legislation documents. The test consists of 3 parts: a preliminary ignition test, a fire penetration test and a spread of flame test. The specimen is subjected to radiant heat and a vacuum is applied to one side to simulate service conditions. A specified flame is applied to the test piece for various durations and the time for the flame to penetrate, as well as the maximum distance of flame spread, are noted. Glowing, flaming, or dripping on the underside of the specimen are also taken into consideration. Results are classified as shown in Table 8 :

The classification is prefixed by Ext. F or Ext. S according to whether the specimen was tested flat or at an inclined plane. The prefix is followed by two letters, the first relating to fire penetration and the second to spread of flame.

Table 8

If the specimen drips on the underside during the test the letter 'X' is added to the two letter code. Thus,

Penetration Time	Spread of Flame
A - more than 1 hour	A - none
B - more than ${}^{1}_{2}$ hour	B - less than 534 mm
C - less than $\frac{1}{2}$ hour	C - more than 534 mm
D - fails preliminary test	D - more than 381 mm in preliminary test

the best possible classification for GRP roof sheeting would be Ext. SAA.

Part 3: 1975 - External Fire Exposure Roof Test

This revision differs from the 1958 version of the standard in the following areas:-

- 1. There is no separate spread of flame test, the extent of surface ignition being measured during the penetration test.
- 2. The duration of the test can be increased if required.
- 3. The number of test specimens is reduced, but their size is increased.
- 4. The test flame is applied several times during the test, instead of only once.
- 5. Performance is not expressed in terms of definite designations, but by actual performance data.

The relationship between the test results is as follows:-

1975

Part 6: 1989 - Fire Propagation Test for Materials

This test measures ease of ignition and the rate of evolution of heat on combustion. Specimens are exposed to direct flame and radiant heat, and the temperature of the hot gases evolved is measured, and compared to a standard non-combustible material (asbestos). Temperature differences at specified intervals are converted into rates of temperature rise and integrated to provide an index of performance I. Certain values for I and sub-index i are currently specified in the UK Building Regulations to classify materials acceptable for use in 'non-combustible' buildings (Class 0).

Part 7: 1997 - Method for Classification of the Surface Spread of flame of Products

In this test, a specimen is mounted at right angles to a radiant panel and heated to a prescribed temperature gradient. A pilot flame is applied to the end of the specimen closest to the radiant panel for the first minute of the test, then removed. The spread of flame is recorded at set distances along the length of the specimen, for the 10 minute duration of the test. Materials are classified according to the flame spread recorded at 1.5 minutes and 10 minutes, as shown in Table 9.

Table 9

Classification	Flame Spread at 1.5 mins.	Final Flame Spread
Class 1	≤ 165 mm	≤ 165 mm
Class 2	≤ 215 mm	≤ 455 mm
Class 3	≤ 265 mm	≤ 710 mm
Class 4	exceeding the limits for Class 3	exceeding the limits for Class 3

Other parts of BS 476 which can be applied to FRP composites, but are not commonly used, are as follows:-

Part 12: 1991 - Method of Test for Ignitability of Products by Direct Flame Impingement

Part 15: 1993 - Method of Measuring the Heat Release of Products

Part 22: 1987 - Methods for Determination of the Fire Resistance of non -loadbearing Elements of Construction

British Standard 6853 - Code of Practice for Fire Precautions in the

Part 13: 1987 - Method of Measuring the Ignitability of Products Subjected to Thermal Irradiance

Design and Construction of Passenger Carrying Trains

This standard advises on best practice in terms of design principles, test methods and performance norms. It includes large scale tests such as the $3m^3$ smoke test.

In today's global market, it has become necessary for the composites industry to produce materials which meet standards of fire performance required by more than one country. Some of these standards are described below:-

American Standards

ASTM E84 - Tunnel Test

This test measures the behaviour of laminates, which form the roof of a tunnel 7.62m long and 0.51m wide. Flame spread results are compared with a scale reading from 0 (asbestos cement board) to 100 (red oak flooring). Fuel contribution and smoke emission properties can also be measured during the test.

UL 94

The Underwriters Laboratory of America carries out this test, which is based on the burning behaviour of small laminate samples (127mm x 12.7mm). The specimens, which can be tested horizontally or vertically, are ignited using a small laboratory burner, and classified according to flame spread and their self extinguishing properties. The first letter of the classification denotes the plane of testing (H- horizontal and V - vertical), with HB being the lowest classification. Vertical classes are V-0, V-1, V-2 and 5V, with 5V being the highest rating. This test is recognised throughout the composites industry.

French Standards

NF P - 92501 - French Epiradiateur Test

This test is carried out in an enclosed cabinet with a chimney at the top. Inside the cabinet is a metal frame which holds the test specimen at an angle of 45° . The specimen is heated by means of a ceramic electric element positioned underneath the sample. The heating element is surrounded by a withdrawable hollow metal cup which collects fumes and vapours and directs them upwards towards a pilot flame at its upper edge. If the pilot light ignites the vapours, the cup is withdrawn, to be replaced if the flames go out. The height of any flames is measured at 30 second intervals during the test, the duration of which is 20 minutes. Throughout the test, the temperature of the incoming and outgoing air/combustibles is measured by sets of thermocouples at the base and in the chimney of the cabinet, and recorded. Materials are classified according to four elements of the test:-

- Ignitability index: i
- Flame development index: s
- Maximum flame length index: h
- Combustibility index: c

Classifications are shown in Table 10:-

		i	h	S	с
M 0	non - combustible				
M 1	non - flammable	0	0	0	<1
M 2	low flammability	<1	<1	<1	<1
	OR	any value	<1	<0.2	<1
M 3	moderately flammable	any value	<1.5 <2.5	<1	<1
	OR	<2	<2.5	<5	<2.5
M4	high flammability				
M5	extremely flammable				

NF F 16 - 101 - Smoke Index Test

This test consists of two parts. Smoke density (Dm) and obscuration (VOF4) are measured using an NBS chamber and a conventional toxicity index (CTI) is calculated from the analysis of gases evolved during combustion (CO, CO2, HCN, HCl, HBr, HF, SO2). Calculations are then carried out using results from these tests, to give a smoke index (IF) classification, as follows :-

IF = Dm + VOF4 + CTI

100 30 2

Classification levels are as follows :-

F 0	-	IF	>	5
F 1			_	20
F 2			_	40
F 3			_	80
F 4			_	120
F 5			_	120
1 5		11		120

International Maritime Organisation (IMO)

The fire performance criteria specified by the IMO are aimed specifically at materials used in marine applications. IMO Resolution A653 (16) as amended by IMO Resolution MSC 61 (67) Annex 1, for instance, measures surface flammability, smoke production and toxicity.

Modifying the burning behaviour of a resin may result in other properties being adversely affected, and it is important to bear this in mind when choosing a resin system to meet specific fire performance criteria. For instance, laminates made using low fire hazard resins generally have poorer weather resistance than normal laminates, so they need the protection of a quality gelcoat if they are to be used externally. Laminates with the best fire performance are often opaque, and most systems of this type are more costly than standard laminates.

The Crystic range of resins and gelcoats designed to perform well in fire situations, covers practically all applications for which resins of this type are likely to be required. Composites produced from these systems are approved to many of the specifications listed in this section, as shown in Tables 11 and 12.

Table 11 - Low fire hazard Crystic resins

	306	323PA	328 PALV	343A	356PA	360PA	385PA	388	1355PA
Features									
Light Stabilised	•	l —	- 1	I —	l —	—	•	•	-
Translucent	•	_	_	I —	—	— I	•	•	-
High Clarity	•	_	_	l —	_	•	_	•	
Filled	_	•	•	•	•	<u> </u>			•
Low Smoke	_	_	_	• •	_	— I		_	- 1
Low Toxicity	_	_	_	•	_	_	_	_	_
Relative Cost	med	low	low	high	med	high	med	high	low
Processes									
Contact Moulding	_	•	•	•	•	•	•	•	•
Closed Mould	_	_	_		-	— I	•	•	•
Continuous	•	_	_	_	_	_	—	•	-
Applications									
Sheeting	•	·	l —	I —	-	—	-	•	-
Roof Domes	•	· _ ·	-	I —	_	— I	•	•	-
Translucent Laminates	•		_	<u> </u>	<u> </u>	•	•	•	
Building Panels		_	•	l —	•	_		_	
Transport		•	_	•	•	_		-	
Approvals									
BS 476: Part 3: 1958	AA	. —	- 1	— I	-	-	AA	AA	- 1
BS 476: Part 6: 1989									
(Class obtainable)	—		l —	0	0	0	-	0	0
BS 476: Part 7: 1997									
(Class Obtainable)	-	2	2	1	1	1	2	1	1
NFP - 92501			l —	M1	— —	—	—	—	-
NFF - 16101		_	_	F0	—	—			-
UL 94		_	_	— ¹	_	_		V-0	_
ASTM E - 84		_	_	I —	35*		25*	25*	_

* According to glass content

Environmental Properties

The ability to withstand normal weathering processes, resistance to water or other chemicals, and the effects of heat, are all critical factors to consider when designing for composites. In the case of glass fibre reinforced polyester, its performance in any environment will be dependent on the actual composition of the laminate, the type of resin used, the surface finish and, most important of all, the degree of cure obtained. It is therefore impossible to provide detailed information covering every variable in the confines of this handbook.

Weather and Water Resistance

The weather and water resistance of GFRP laminates is largely a function of the gelcoat since in most applications this is the surface which is exposed to attack. Where general resistance to weather or water at ambient temperature is the main criterion, a quality isophthalic gelcoat will give adequate protection, but where hot water and/or mild chemicals are involved, an iso/NPG based gelcoat is recommended. In some applications (e.g. roof sheeting) the use of a gelcoat is not practical, and in these circumstances, it is important to use resins from the Crystic range, which have been specially developed to withstand the effects of UV radiation and water.

Fire retardant laminates present unique challenges in terms of their weather resistance. Without the protection of a gelcoat their resistance to outdoor exposure is poorer than that of standard laminate

SYSTEM		B.S. 476			Epiradiateur		
	Part 3: 1958	Part 6: 1989	Part 7: 1997	NFP 92501	NFF 16101		
GC 39PA + C.323PA + C.356PA + C.385PA + C.1355PA	 FAA 		Class 2 Class 1 Class 2				
GC 48PA + C.323PA + C.328PA + C.326PA + C.356PA + C.385PA + C.1355PA		 Class 0 	Class 2 Class 2 Class 1 Class 2	 M 2	 F 3	 HB V - 0	
GC 65PA + C.356PA + C.360PA + C.1355PA	 FAA	Class 0 	Class 1 Class 2 Class 2	M 1 M 2	F 3 	 V - 0	
Fireguard 75PA* + C.405PA + C.1355PA		Class 0	Class 1 Class1				
GC 90PA + C.356PA + C.360PA + C.1355PA		Class 0 	Class 1 Class 2 Class 2				
GC 93PA + C.356PA + C.1355PA		Class 0	Class 1				

* Intumescent flowcoat

of a gelcoat can adversely affect the fire performance of such laminates.

The Crystic range includes a resin which has such excellent fire retarding properties, that a standard isophthalic gelcoat with proven weathering performance can be used with no reduction in fire rating.

Long term immersion in water can result in a loss of mechanical properties, especially where a laminate is not protected by a gelcoat. Table 13 shows the effects of long term immersion on the flexural strength of orthophthalic polyester resin/glass mat laminates with sealed and unsealed edges, but no gelcoat.

Figures 12 to 14 show various effects of weathering on GFRP composites.

Chemical Resistance

For mouldings with optimum chemical resistance combined with high structural performance, a resin rich surface is essential on the face which is to be exposed to the hostile environment, and this should be accompanied by a chemical resistant laminating resin. A resin rich surface can be achieved by the use of a gelcoat, or for contact with more aggressive environments, by means of resistant surfacing veils which take up large quantities of resin. The most suitable laminating resin will depend on the particular chemical environment, but generally, orthophthalic resins have good resistance to acidic conditions, whilst alkaline conditions require the improved resistance of isophthalic or iso/NPG systems. Bisphenol based polyester resins exhibit high mechanical strength and excellent strength retention in many chemical environments at temperatures up to 95°C. Vinyl ester resins and epoxide resins are also widely used in the chemical containment industry. The type of surfacing veil to be used will also differ with the type of chemical involved. Polyester veils are recommended for acidic conditions, whilst polyacrylonitrile veils are more resistant to alkaline environments.

Although the chemical resistance of fully cured polyester resins is generally good, there are other plastic materials which are more resistant to certain chemical environments. These can be used to produce a composite construction in which the mechanical strength is provided by a GRP laminate and the chemical resistance by a thermoplastic liner such as PVC or scrim - backed polypropylene. An important example of this type of composite construction is the filament winding or wrapping of PVC pipes with glass rovings and resin, and tanks and pipes for the chemical industry are commonly made in this way.

Specialist Crystic resins have been developed for this application and the Crystic range contains resins which are suitable for use in many chemical environments. These are fully detailed in a separate publication 'Safe Chemical Containment '.

General standards for the design, fabrication and use of vessels and tanks in GFRP composites are laid down in BS 4994: 1987 entitled 'Specification for Vessels and Tanks in Reinforced Plastics'. (see Appendix 1). A new European Standard, pr EN 13121, is currently being developed, and may eventually replace BS 4994:1987.

Table 13 - Strength retention of FRP composite* after immersion in distilled water at 20°C

Immersion Time	Unsealed E	Edges	Sealed Edges		
	Bend Strength	Retention	Bend Strength	Retention	
Days	MPa	%	MPa	%	
0	204	, '	204		
7	192	94	199	98	
28	186	91	193	95	
63	182	89	190	93	
112	181	89	190	93	
300	181	89	190	93	

* Acid Resistant Orthophthalic Polyester Resin / Glass Mat Laminate

Figure 12 - Effect of weathering on the light transmission of GFRP sheeting at various resin contents

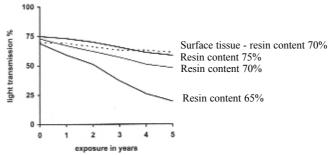
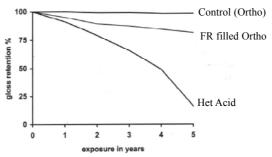
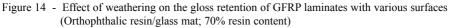
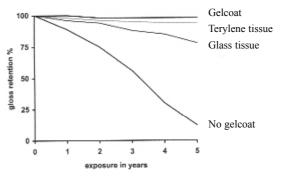


Figure 13 - Effect of weathering on the gloss retention of low fire hazard GFRP laminates with gelcoats







QUALITY CONTROL

Quality Control

The essential difference between FRP composites and almost all other structural materials is that, whilst the chemical composition and properties of other materials e.g. steel or aluminium, are mainly determined by the manufacturer, with reinforced plastics the fabricator determines these properties himself i.e. he makes his own material.

Quality control is therefore extremely important if high quality mouldings are to be produced consistently, economically and safely. This section deals with aspects of quality control from the storage of materials through the various stages of moulding production to the delivery of quality moulded parts.

Storage

Resins, curing agents and associated solvents should be stored separately, in cool, dry, well ventilated places away from the working area.

Resin should be stored in the dark in suitable closed containers. It is recommended that the storage temperature should be less than 20°C where practical, but should not exceed 30°C. Ideally, containers should be opened only immediately prior to use, and should never be left open. Where containers have to be stored outside, they should be protected from the elements to prevent any ingress of water, or possible early polymerisation from the effects of direct sunlight.

After several months or years of storage, polyester resins will set to a rubbery gel, even at normal ambient temperatures. This storage life or shelf life varies depending on the resin type, but provided that the recommendations above are followed, most Crystic resins will have a storage life of at least 3 months (for pre-accelerated resins) or 6 months (for non-accelerated resins).

Organic peroxide catalysts should be segregated from resins and accelerators. Containers should be stored in a well ventilated, flameproof area at a maximum temperature of 20°C. Bulk storage should ideally be in a secure brick building, but smaller quantities can be stored in suitable metal cabinets. Containers should be opened only immediately prior to use, and should never be left open.

Accelerators should be stored in a well ventilated, flameproof area at a maximum temperature of 20°C. Containers should be opened only immediately prior to use and should never be left open.

All storage areas should be kept clean and free from combustible materials such as rags. Good standards of hygiene should be observed and SMOKING MUST BE PROHIBITED. Any accidental spillages **must** be dealt with immediately.

Reinforcements can be kept in the main workshop as long as they are stored and tailored away from the moulding area. All reinforcements should be stored in their original packaging in a warm, dry, dust free environment.

Stock Control

All containers and packaging should be appropriately marked, designated and documented. Good stock control is important as the use of stocks in strict rotation helps to avoid storage times longer than the manufacturer recommends, thus ensuring that materials are always used in their optimum condition.

Workshop Conditions

Any building where composite manufacturing is carried out should be dry, adequately heated and well ventilated. Ideally, the building should be spacious, to allow adequate room for all operations, and have a high ceiling.

The temperature of the building should be controlled between 15° C and 25° C, at all times, and fluctuations in temperature must be avoided.

Ventilation should be good by normal standards, but draughts should be avoided. Doors and windows should not, therefore, be used for ventilation control.

Although diffused daylight lighting is the preferred type, fluorescent lighting is an acceptable alternative and is most commonly used.

The working area should be divided into sections as follows:-

1. Preparation of Reinforcement

It is important to tailor reinforcing fibres in a cool, dry environment away from the general moulding and trimming / finishing areas. Moisture and dust must be avoided as they may affect the moulding characteristics of the reinforcement, resulting in poor quality mouldings.

2. Compounding & Mixing of Resins

The compounding and/or mixing of resins is best kept to a separate section of the workshop, preferably in the charge of one responsible person. Accurate weighing apparatus and a low shear mechanical mixer are required, as well as suitable catalyst dispensing equipment. If accelerators and catalyst are to be added, separate dispensers must be used as **catalyst and accelerator can react with explosive violence**. All measuring and mixing should be restricted to this one area, which should be kept as clean as possible to prevent contamination.

3. Mould Preparation and Moulding

The layout of the workshop can be fairly flexible to allow for different types and sizes of moulding. As with most other kinds of manufacturing operations, it is best for the operators to remain in one place and the moulds to move from station to station as the moulding operation is completed, although this is not always possible.

It is important to keep moulds away from direct sunlight, as this may cause premature gelation of the resin. Any fluorescent lighting should be installed as far above the moulds as possible, as it can also affect the cure of the resin. Cleanliness is important for the health of the operators and for preventing contamination of resin and reinforcement. Containers of resin, solvents, etc. must not be left open. Any spillages should be attended to immediately and contaminated waste material should be removed and disposed of safely.

The Health & Safety at Work Act has specific requirements for the control of the working atmosphere and in particular, attention should be paid to the concentration of styrene vapour in moulding shops. Developments in resin technology mean that resins with low styrene emissions and low styrene contents, such as those in the Crystic range, are now available. Although these resins significantly reduce the amount of styrene in the atmosphere during lamination and consolidation, adequate extraction facilities are still essential in this area of the workshop.

4. Trimming and finishing

Effective dust extraction is essential in this area of the workshop, and should preferably be of the down draught type. A good standard of cleanliness is also important, to prevent contamination of partly cured mouldings.

Mould Care

The production of quality composite mouldings will depend to a great extent on the quality of the moulds used for their manufacture. It is therefore important to ensure that moulds are properly maintained throughout their life. Moulds should be cleaned regularly, particularly where wax release agents are used, as any wax build up may result in a dulling of the mould surface. This will then transfer to the surface of the moulding, creating dull areas which are difficult, if not impossible, to remove.

Impacting the back surface of a mould in order to remove a moulding is not recommended as it can result in cracking of the gelcoated surface of the mould. Whilst these cracks will not affect the mould structure, they are unsightly and will transfer to the surface of any mouldings taken from the mould.

Great care should be taken when repairing any damage to moulds, particularly in the gelcoat surface, and repairs should be carried out as soon as is practical after the damage occurs. The development of mould re-surfacing products, such as those in the Crystic range, means that the life of moulds can now be extended even if the gelcoat is damaged beyond repair.

Resin Usage

The Curing Reaction

Different resin types exhibit different cure characteristics, but whichever resin type is being used, it is important that the recommended cure cycle is followed.

The cure of a polyester resin will begin as soon as a suitable catalyst is added, but the speed of cure will depend on the resin and the activity of the catalyst. Without the presence of an accelerator, heat or ultra violet radiation, the catalysed resin will have a pot life of hours or sometimes days. This rate of cure is too slow for practical purposes, so for room temperature conditions an accelerator is used to speed up the reaction. Although these days the vast majority of resins are pre-accelerated by the manufacturer, some of the more specialised resin systems still require the addition of an accelerator to facilitate cure. In these cases, the quantity of accelerator added will control the time to gelation and the rate of hardening. For many of today's processes, the limited pot life of a catalysed resin is impractical, and in these instances it is advisable to add the accelerator to the resin first. The accelerated resin will remain usable for days or even weeks, and quantities can be catalysed as and when required.

The curing reaction of a polyester resin is exothermic, and the temperature of an unfilled resin casting can rise to over 150°C, though this temperature rise would be considerably less in a laminate. The resins and catalysts available today have been specially developed to dramatically reduce exotherm temperatures, enabling moulders to produce larger and thicker composite structures without the problems associated with heat build up.

Figure 15 illustrates the exotherm characteristics of a typical polyester resin.

There are three distinct phases in the curing reaction of a polyester resin :

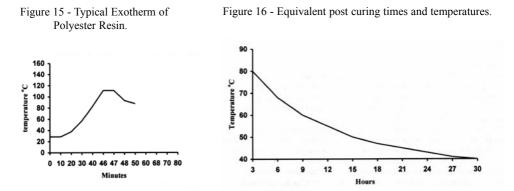
- 1. **Gel time**. This is the time between the addition of the curing agent (catalyst or accelerator/catalyst) and the setting of the resin to a soft gel.
- 2. **Hardening Time**. This is the time from the setting of the resin to the point where the resin is hard enough to allow a moulding to be released from its mould.
- 3. **Maturing Time**. This is the time taken for the moulding or laminate to acquire its full hardness, chemical resistance and stability, and can vary from hours to days to weeks depending on the resin and the curing system used. Maturing will take place at room temperature, but post curing a moulding at elevated temperatures will accelerate this process.

When post curing is used, it is recommended that the moulding is allowed to mature at room temperature for a period of 24 hours before exposure to elevated temperatures. Figure 16 shows equivalent post cure times and temperatures. Resin properties are improved by post curing. For critical applications such as those requiring maximum heat resistance, post curing is essential, preferably by increasing temperature in stages up to the required operating temperature.

Hot Curing

Polyester resins are often hot moulded in the form of dough or sheet moulding compounds, or in continuous processes such as pultrusion (see Processes section). However, a simple hot moulding formulation is possible, using benzoyl peroxide as the catalyst. These catalysts, which normally contain 50% benzoyl peroxide, are available in powder or paste form, and should be added at 2% into the resin. The catalyst must be thoroughly dispersed in the resin, and the catalysed mix will remain usable for about a week at room temperature (18°C to 20°C).

Cure should take place at temperatures between 80°C and 140°C, but for most applications, 120°C will be satisfactory. The actual moulding time will depend on the bulk or thickness of the moulding, the type of resin used, and the heat capacity of the moulds. Insufficient heat or time will result in an undercured

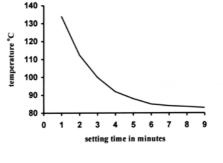


moulding. Whilst the resin cannot be over cured, it is not advisable to raise the temperature above 140°C. The influence of moulding temperature on the setting time of a typical polyester resin is shown in Figure 17.

Figure 17 - Hot curing of a Typical Polyester Resin Using 2% Benzoyl Peroxide Catalyst.

Cold Curing

The great majority of manufactured using adequate cure is vital if optimum properties are to Most of today's polyester and require only the to initiate the curing



composite mouldings are cold cure techniques, and high quality mouldings with be produced. resins are pre-accelerated, addition of a suitable catalyst reaction, though some more

specialised resins still require the addition of an accelerator as well as a catalyst. Cobalt accelerators are the most common, though others, such as those based on tertiary amines, are also used. The most common cold curing catalysts are methyl ethyl ketone peroxides (MEKP). These are supplied as liquid dispersions differing only in their activity, reactivity and hardening rates. Cyclohexanone peroxide (CHP), available as a stable paste dispersion, and acetyl acetone peroxide (AAP), are also widely used in applications where their effect on cure characteristics are more appropriate.

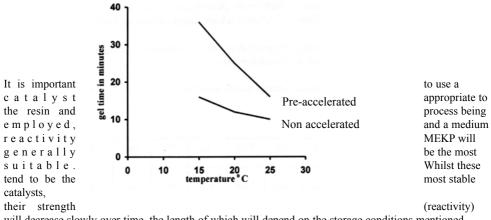
Table 14 shows the gelation and hardening characteristics of the more commonly used catalysts. Curing should not be carried out at temperatures lower than 15°C as this can result in undercure. The effect of ambient temperature on the gel time of typical orthophthalic polyester resins is shown in Figure 18.

Table 15 illustrates the importance of correct catalyst choice and addition levels by showing the affect on hardening rate of various catalyst types and levels in a typical orthophthalic polyester resin.

Table 14 - Cold curing catalysts

	Typical % on weight of resin	Affect on geltime	Affect on hardening rate	Other remarks
CHP Paste	4	slow gelling	rapid hardening	for all high quality applications
Low Reactivity MEKP	2	slow gelling	medium hardening	for optimum properties after post cure
Med. Reactivity MEKP	2	medium gelling	medium hardening	good stability
High Reactivity MEKP	1	rapid gelling	medium hardening	cheapest because of high potency
AAP Liquid	2	medium gelling	rapid hardening	suitable for closed mould processes

Figure 18 - Effect of ambient temperature on the gel time of a typical polyester resin



will decrease slowly over time, the length of which will depend on the storage conditions mentioned

Table 15 - Effect of catalyst on the hardening rate of a typical orthophthalic polyester resin

Catalyst	Addition Level	Hours after gelation									
		1	2	3	4	5	6	7	24	48	168
					Barcol	Hardn	ess (G	YZJ 93	4 – 1)		
CHP											
	4%	0	6	17	20	22	24	26	38	43	55
MEKP											
(Med. React.)	2%	0	0	6	15	19	21	23	37	42	55
MEKP											
(high react.)	2%	0	5	16	21	25	26	27	38	44	54
MEKP											
(high react.)	1%	0	0	3	8	14	18	20	36	42	53

earlier. It is important from a quality point of view, that catalyst is fresh when used, as its characteristics will change completely after long storage. Low reactivity MEKP should not be used at temperatures below 15°C.

Factors Affecting Geltime

The following factors can influence the geltime and therefore the final state of cure of polyester resins, including those in the Crystic range.

- Catalyst content. The less catalyst used, the longer the geltime. Insufficient catalyst leads to undercured mouldings.
- Accelerator content. If non accelerated resins are used, the accelerator content must be sufficient to
 activate the catalyst or the resin may remain undercured, or harden too slowly.
- Ambient temperature. The lower the temperature, the longer the geltime. Curing below 15°C is not recommended as it can lead to undercure.
- Bulk of resin. The larger the bulk of resin the faster the geltime. For example, a 25mm cube of resin will set faster than a 2mm thick laminate, using the same formulation.
- Loss of monomer by evaporation. Insufficient monomer in the resin will result in inadequate polymerisation. A fast geltime will minimise evaporation.
- Use of fillers. Most fillers will extend the geltime of a resin, and as a general rule, mineral filler content should be kept as low as possible.
- Pigment content. Some pigments lengthen geltime, others can shorten it, so only pigments specifically designed for polyester resins should be used.
- Presence of inhibitors. Some compounds, even in trace amounts, can inhibit the cure of polyester resins and may prevent full cure altogether. Common inhibitors are phenols (present in phenolic resins), phenol formaldehyde dust (present in melamine), sulphur, rubber, copper and copper salts, carbon black and methanol.
- Mixing. All component materials must be thoroughly dispersed in the resin. Inadequate mixing of catalyst and/or accelerators can lead to patchy cure and moulding faults.

Table 16 shows appropriate catalyst/accelerator levels for various quantities of resin.

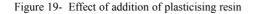
Effect of Additives on Resin Properties

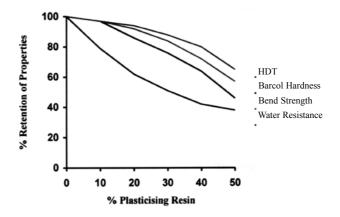
Additives can have an adverse effect on the properties of polyester resins and care should always be taken

Resin wt.		lkg	2kg	3kg	4kg	5kg	6kg	7kg	8kg	9kg	10kg
Pastes 4%	g	40	80	120	160	200	240	280	320	360	400
Powders 2%	g	20	40	60	80	100	120	140	160	180	200
Liquids 1% 2% 3% 4%	ml ml ml ml	10 20 30 40	20 40 60 80	30 60 90 120	40 80 120 160	50 100 150 200	60 120 180 240	70 140 210 280	80 160 240 320	90 180 270 360	100 200 300 400

resin they are to be used with. Pigments and fillers which have been specifically developed for use with polyester resins should always be used where possible.

In some instances, it may be desirable to blend resins together to achieve specific properties, but it is important to bear in mind that properties cannot be changed in isolation. For example, in some applications, plasticising resins are added to standard resins to increase levels of flexibility and reduce brittleness. Whilst these additions increase toughness and resilience, they will adversely affect other properties, as shown in Figure 19.





Common Faults

This section has covered all aspects of the quality control of FRP composite manufacture, and provided

that the recommended procedures are followed, high quality FRP mouldings will be produced consistently. However, from time to time problems will occur, and some of the more common faults and their causes are outlined here.

WRINKLING

- Insufficient cure
- Gelcoat too thin
- Back-up too rapid
- Catalyst contamination
- Solvent attack

POROSITY

Pinholes

- Gelcoat too viscous to release air
- Cold gelcoat and/or mould
- Poor mixing
- Gelled too quickly, entrapping air

Voids in film

- Incorrect catalyst
- Poor spraying
- Entrapped water, solvent or oil
- Incorrect rheology
- Unsuitable spray gun

GELCOAT PEELING

- Contamination
- Gelcoat too fully cured
- Geltime too long release wax dissolved
- Excessive release wax
- Dry reinforcement

PRE-RELEASE

- Uneven gelcoat cure
- Gelcoat too fully cured
- Catalyst level too high
- Styrene content too high
- Inappropriate mould release system
- Heat and movement from rapid laminate cure
- Mould movement

DE-WETTING, 'FISH EYES'

- Gelcoat too thin
- Viscosity too low
- Release system
- Contamination (water, oil, silicones, gelled resin particles)

POCK MARKS

- Gelcoat contamination
- Foreign matter on mould surface
- Overspray
- Dry laminate
- Air voids in laminate
- Excess or large binder particles in reinforcing mat

COLOUR SEPARATION

- Dirty equipment
- Contamination
- Insufficient mixing
- Sagging, drainage
- Poor gelcoat application
- Gelcoat dilution
- Unsuitable pigments

COLOUR TEARING

- Pigment separated from resin
- Improper spray technique
- Long geltime, sagging

COLOUR SPECKS

- Poorly ground/mixed pigments
- Contamination

DIMPLING

- Too heavy wet on wet spray application
- Insufficient consolidation

SAGGING

- Gelcoat too thick
- Geltime too long
- Temperature too high
- Viscosity/thixotropy too low
- Unsuitable pigment paste
- Mould movement

DULL SURFACE

When released

- Incorrectly used wax
- Wax build-up
- Unsuitable release wax
- Poor mould surface
- Polystyrene build-up •
- Dust on mould
- Condensation on mould
- Wet or rough PVA film

In patches

- Water on mould or in gelcoat
- Uneven gelcoat
- Poorly mixed catalyst
- Uneven wax application
- Undercured mould gelcoat

After release

Insufficiently cured gelcoat

- Undercure
- Unsuitable environment

CHALKING

- Undercure
- Surface grime
- Unsuitable pigment/carrier
- Excessive pigment/carrier
- Chemical attack

FIBRE PATTERN

- Transferred from mould
- Gelcoat too thin
- Cloth or woven roving too close to surface
- High exotherm in laminate.
- Insufficient cure, released too soon

CRACKING

• Poor de-mould technique

Star cracks

- Reverse impact • Gelcoat too thick
- Crack pattern transferred from mould

Parallel cracks

- Flex cracking
- Gelcoat too thick
- Poor mould release
- Laminate too thin
- Laminate too flexible

Crazing/small groups

- Chemical/hot water attack
- Incompatible liquid, 'blowing' in service

BLISTERS

On release

- Air voids
- Unreacted catalyst
- Solvent contamination

In water

- Air voids
- Osmotic reaction

SOFT GELCOAT

- Undercured
- Too much filler or pigment
- Unsuitable filler or pigment
- Temperature too low when moulded
- Temperature too high when hardness tested

'WATER MARKING' 'ETCHING ON MOULD'

- Areas of thin, double gelcoating on mould
- Two colours gelcoated on mould
- Solvent attack

Repair

Some moulding faults can be rectified at the trimming finishing stage of production. Cracks, dents and small holes in the gelcoat surface can be repaired using

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and

gelcoat filler (such as that in the Crystic range), a mixture of lay - up resin and filler powder or, where better 'gap-filling' properties are required, a repair dough consisting of resin and chopped glass fibre strands.

Repairing Gelcoat Scratches

- 1. Ensure the damaged area is clean, dry and free of oil, wax or grease, then tape round with masking tape to protect the surrounding surface.
- 2. Mix the required quantity of gelcoat filler and pigment paste thoroughly.
- 3. Add the appropriate amount of hardener and mix thoroughly.
- 4. Using a wooden spatula, press the gelcoat filler firmly into the scratch, filling proud of the surface. Remove the masking tape before the filler sets, and leave to cure thoroughly for at least two hours.
- 4. When cured, rub down with wet and dry paper then use polishing compound to restore the surface gloss.

Filling Dents and Cracks

Cracks, dents and even small holes can be repaired using mixtures of lay-up resin and fillers. Care should be taken to use a filler appropriate to the application - in boat hulls for instance, glass bubbles should be used as most other fillers absorb water.

- 1. Remove any loose resin and reinforcement and ensure the damaged area is clean, dry and free of grease.
- 2. Mix pigmented resin with filler powder or glass fibres until a paste of the required consistency is achieved.
- 3. Add the correct amount of hardener (based on resin weight NOT resin/ filler weight).
- 4. Tape around the damaged area then fill the dent using the resin/filler or resin/glass fibre mix.

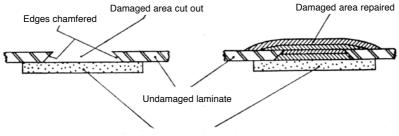
5. Leave to harden, then sand using progressively finer grades of wet and dry paper, and use polishing compound to restore surface gloss.

Repairing Laminate Damage

When damage is not confined to the surface, resin and reinforcement should be laid up, overlapping the edges to ensure good adhesion over a wide area.

If the laminate is fractured, the following procedure should be used, to effect a repair.

- 1. Remove the damaged area and chamfer the edges so that the hole is larger on the gelcoat side than on the reverse.
- 2. Abrade and clean the surrounding area to ensure adhesion.
- 3. If a large surface area is involved, a temporary mould should be built up on the exterior surface (see Figure 21). For smaller areas, polyester release film can be used as a moulding surface.
- 4. Where damage is extensive, the moulding should be placed in its original mould before repairs are carried out.



Temporary mould or release film

and FRP composite fabrication, is that with FRP, the fabricator makes his own raw material. He therefore needs to understand the nature of FRP composite structures as well as the importance of the various stages of fabrication.

It is extremely important, therefore, that inspection takes place at every stage of fabrication. It is vital to eliminate as many variables as possible and to ensure consistency, both in materials and fabrication processes.

The visual inspection of mouldings should scrutinise the following:-

- Surface imperfections and general appearance.
- Entrapment of air bubbles in the laminate. The use of non- pigmented resins facilitates this inspection.
- Dimensions assessment of any shrinkage or distortion.

The physical testing of laminates, i.e. mechanical and chemical testing, can be a problem for the fabricator, as it involves the use of specialised test equipment. These tests are, therefore, normally carried out by either the raw material supplier or independent test houses. The properties considered to be of most importance are:-

- Ultimate tensile strength
- Tensile modulus
- Flexural strength (also known as bend or cross breaking strength)
- Modulus in bend
- Impact strength
- Shear strength

None of these properties should be considered in isolation. For instance, it is possible, by using a high glass content, to produce a laminate with a high tensile strength. However, such a laminate would be so thin that it would lack rigidity, so would be unsuitable for use. Minimum thickness and resin to glass ratios are therefore also important properties.

Resin to Glass Ratios

Resin to glass ratio has more affect on the physical properties of a fully cured laminate than any other single factor. As a general guide, a high glass content will result in a high strength laminate, whilst a high resin content will produce a laminate with better chemical, water and weather resistance.

The resin to glass ratio is found by weighing a small piece of laminate - one centimetre square would be sufficient - in a crucible, ashing it over a bunsen burner, and re-weighing it once it has cooled. This is a simple test which requires little in terms of equipment, but is valuable in terms of quality control.

Degree of Cure

Some variability in properties can be caused by differences in the degree of cure of a resin. Severe undercure in a laminate will be obvious since the laminate will be noticeably soft, and will have a characteristic smell reminiscent of almonds. Slight undercure, however, is often more difficult to detect, and whilst there may be little or no affect on mechanical properties, undercured laminates exposed to weather will deteriorate rapidly.

A surface hardness test is the most practical method of assessing degree of cure under workshop conditions, and the best instrument for measuring this is a Barcol Impressor. Although Barcol hardness is not an absolute measure of cure, it can highlight differences between well cured and poorly cured laminates. Fully cured, unfilled cast polyester resins generally exhibit a Barcol hardness figure between 40 and 50 (35 to 45 for gelcoat resins), and average readings of less than 25 on a laminate would suggest undercure.

Control of Variables

FRP composites are not homogeneous structures, so there is the potential for a considerable degree of variability in their physical properties. These variations can be kept to a minimum by controlling certain factors during manufacture.

- Resin content. Variations in resin content will lead to variations in final properties. Adequate consolidation of the reinforcement will minimise resin content differences.
- Geltime. Excessively long geltimes can lead to styrene loss through evaporation, and this can result in undercure.
- Ambient temperature. This should be kept constant, ideally in the range 17°C to 23°C. Draughts should be avoided as these can cause excessive styrene loss, leading to undercure.
- Quantity and mixing of curing agents. Accurate additions, and thorough mixing of curing agents is essential, to ensure consistency of cure.

Investing in the quality control methods and procedures outlined here will enable the consistent production of high grade FRP composites both economically and safely.

MOULD (TOOL) MAKING

The Importance of Tooling

Tool design and production must be given careful consideration if high quality mouldings are to be produced

consistently - any moulding will be only as good as the mould it is taken from.

Contact Moulding is the main open mould process, utilising either hand, spray or roller saturation lay-up techniques. As described earlier (see Processes Section), only one mould is needed for contact moulding, and in most cases the mould, as well as the mouldings, will be manufactured using FRP composite materials.

Closed mould processes such as VI, VacFlo and RTM can also utilise composite tooling, though more care has to be taken in tool choice and design.

As with contact moulding, VI requires only one mould, though additional edge detail may be required. Higher quality mould making materials may be needed, in order to accommodate the higher exotherm temperatures often generated in thicker sections.

VacFlo moulds require more care in construction than those for VI, as they need two matched moulds with an accurate cavity. Flange detail must give easy, reliable closing whilst maintaining vacuum integrity. The main advantage of composite VacFlo moulds is that they are light in weight, and coupled with the fact that vacuum provides the closing force, this means that no heavy press or rigid framework is required.

Tooling for RTM can involve considerably more investment than that for VI or VacFlo, as it is more demanding in its requirements. A rigid mould is essential to prevent distortion during the injection process, and to control the accuracy of the moulded part. The mould must also be durable and able to resist chemical and heat attack over a life of hundreds or thousands of mouldings. There are many materials which can be used to manufacture RTM moulds. The material chosen will depend on several factors such as component shape, numbers off, cost, production rate, etc. Table 17 shows the various options and their advantages / limitations.

Moulds for cold and warm press moulding have similar requirements to those for RTM. It is most important that the mould cavity is accurately defined, and does not distort under pressure. Composite tooling, mounted onto the platen of a press, can be used in these processes, but moulds must be resistant to heat, and durable over long production runs.

Table 17 - Materials f	for RTM tooling
------------------------	-----------------

Hot press moulding is normally used for high volume production using

Material Type	Comments
Polyester Based Composite	Mainly used for prototypes or short production runs. Ambient temperature tooling only.
Vinyl Ester / Epoxy Based Composite	Stronger, tougher & more temperature resistant than polyesters. Temperature controlled tooling is recommended.
Kirksite (Zinc Alloy)	Low cost metal tooling, though relatively low strength and hardness. Shorter life expectancy than other metals. Generally temperature controlled tooling.
Cast Aluminium	Prone to surface porosity. Surface easily damaged. Generally temperature controlled tooling.
Metal Spray	Low cost metal tooling. Less durable than other metal surfaces. Generally temperature controlled tooling.
Electroformed Nickel Shell	Most popular metal tooling option. Has potential for Class 'A' surface finish. Life in excess of 100,000 parts. Particularly suited to more complex shapes. Generally temperature controlled tooling.
Steel	Only chosen for very long production runs. Generally temperature controlled tooling.

materials such as SMC or DMC. Highly polished matched metal dies are normally used in these processes, due to the high temperatures and pressures involved.

Continuous processes such as pultrusion and filament winding, tend not to utilise composite tooling. Most continuous processes involve considerable investment in terms of machinery and equipment, and are used for constant production. Tooling has to be accurate, resistant to heat and chemical attack and extremely durable. Metal tooling is therefore most suited to these processes.

Producing Composite Mould Tools

The selection of suitable materials and build procedures is vital for ensuring good surface finish, stability and longevity of composite mould tools. Each mould manufacturer will have a preferred method of mould construction. For instance, some will use cored structures, others solid laminates; some will incorporate steel stiffening, others will use FRP stiffeners. Whatever methods are employed, there are some basic principles which must be followed if a high quality mould is to be produced.

Plug Production

The importance of plug quality cannot be over emphasised, as it will ultimately determine the quality of the mould and, from that, the final moulding.

A plug should be accurately made and dimensionally stable. It should be set on a firm foundation, and not moved until the mould is complete. Temperature should be controlled between 18°C and 23°C, humidity should be constant, and the plug should not be subjected to direct sunlight. Plugs can be manufactured from a variety of disparate materials including timber, plywood, MDF and polyester filler, and fluctuations in temperature and humidity will have an adverse effect on dimensional stability.

It is important that there are no irregularities in the plug surface, as these will transfer to the mould surface and be difficult to remove. The plug surface should be styrene resistant, and of the same gloss level as is required from the mould itself.

The development of high build polyester coatings, such as those in the Crystic range, allow the rapid surfacing of plugs constructed from a variety of materials such as wood, MDF or FRP. These materials are sprayed onto the plug surface after it has been abraded and de-greased. They harden rapidly and when cured, can be easily sanded to a very smooth finish which is then polished. Different gloss levels can be achieved, depending on the requirements of the mould.

Once a plug is complete, FRP moulds can be produced from it easily and quickly and a well prepared plug will minimise any remedial work required on moulds taken from it.

A suitable release agent should be applied to the plug before moulds are produced from it. The Crystic range contains several types of release agent, from waxes through to semi-permanent systems. Whichever type is chosen, it is important to apply it according to the recommended procedure.

Having carefully prepared the plug, mould production can begin, and it is important at this stage to use materials and procedures designed and recommended for the manufacture of FRP composite moulds.

Mould Making Materials

Scott Bader's Crystic range contains gelcoats and resins developed specifically for the production of high quality FRP moulds.

Gelcoat

A mould making gelcoat needs to be resilient, heat resistant and solvent resistant with the ability to polish to a high gloss.

It is extremely important that the gelcoat is applied correctly, if problems such as water marking or dulling of the surface are to be avoided.

The gelcoat, mould and workshop should all be at, or above, 15°C before curing is carried out. A medium reactivity MEKP catalyst is recommended for curing the gelcoat, at an addition level of 2%.

The gelcoat application should be controlled at a wet film thickness of 0.5mm - 0.6mm. This will allow for any rubbing down which may be necessary during the life of the mould. Thin gelcoat (i.e. less than 0.4mm) may lead to styrene loss, resulting in undercure and possible water marking in service.

Laminating Resin

A reactive, temperature resistant, orthophthalic polyester resin is recommended for the backing laminate, as this will ensure a stable mould structure. The use of a resin with high reactivity makes it advantageous to add up to 25 parts per hundred (20% by weight) of a suitable filler such as a calcium magnesium carbonate (dolomite) during certain stages of mould production. This will reduce exotherm on cure and also lessen shrinkage.

A medium reactivity MEKP catalyst should be used to cure the resin, at a minimum addition level of 1%. If a longer working time is required, a lower reactivity catalyst should be used, rather than reducing addition levels below 1%.

Reinforcements

Chopped strand glass mat is generally the preferred reinforcement for mould manufacture. Where woven materials are used, great care must be excercised to ensure that print-through does not occur. Proprietary materials designed to prevent or reduce print through are available, and their use at a suitable point in the laminate can alleviate the problem.

For stiffness without excessive weight, balsa or foam cores can be incorporated into the mould. Core materials can also prevent print-through, particularly where the supporting structure is attached to the mould shell.

Workshop Conditions

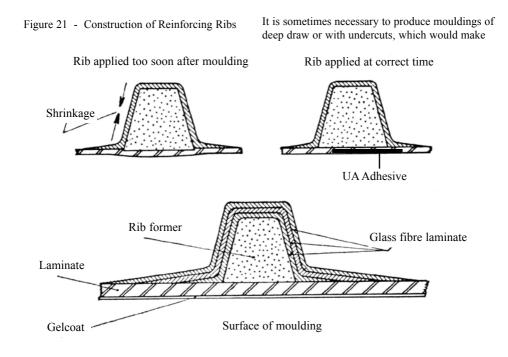
The workshop used for plug and mould manufacture should be well ventilated and, as far as possible, controlled at temperatures between 18°C and 23°C, with 18°C being the absolute minimum. Temperature should be monitored using a maximum/minimum thermometer. Humidity should be as constant as possible, and the plug should be positioned out of direct sunlight.

All materials should be stabilised at workshop conditions before construction starts, and any fillers should be kept dry.

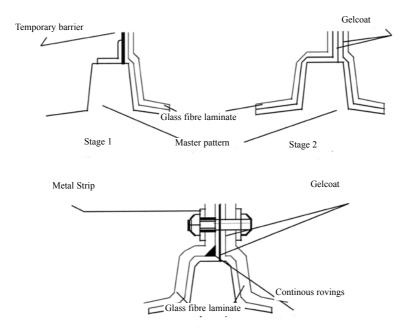
Mould Construction

Mould construction should not be rushed. It is important to build the mould in such a way as to eliminate excessive temperature build up during laminating, and to ensure that the mould is well cured before releasing it from the plug and putting it into service.

Large moulds may require extra stiffening, and this can be achieved by adding stiffening ribs to the reverse side of the mould. Formers are shaped to the contours of the mould, placed in position and laminated over using two or three layers of resin and glass. The materials used for the formers can be solid timber or metal, hollow metal or plastic piping, foamed plastic, paper rope; in fact virtually any material which can be suitably shaped. Before the ribs are built into the mould, the laminate itself must be fully cured and of adequate thickness, or contraction of the resin around the ribs may distort the laminate and leave an impression (sink mark) on the mould surface. Holding formers in place with adhesives such as those in the Crestomer range, can eliminate the incidence of sink marks provided the adhesive is applied correctly. (see Figure 21).



release from a one piece mould difficult or impossible. A split mould is therefore essential. A good example of this is in the production of large boat hulls where the mould is generally split down the keel line. The construction of flanges for split moulds is shown in Figure 22.



localised loads imposed by nuts and bolts or clamps, and for this reason, they should be made 50% thicker than the mould shell. It is also best to fix metal plates along the flanges so that fixings can be made every 150mm or so, to hold the two halves of the mould together.

The following is an example of a build sequence which has been shown to produce high quality moulds with a minimum of distortion:

- Day 1: Apply 1 layer clear gelcoat and 1 layer black gelcoat Apply 1 layer surface tissue using unfilled resin Day 2: Apply 1 layer 300g/m² CSM using unfilled resin Day 3: Apply 1 layer 600g/m² CSM using filled resin Day 4: Day 5: Apply 1 layer 600g/m² CSM using filled resin. Allow to exotherm. Apply 1 layer 600g/m² CSM using filled resin To prevent print through from any subsequent core or woven material, apply 1 layer Day 6:
- 450g/m² CSM and allow to exotherm. Apply 1 layer 2mm non-woven core material or print-stop fabric
- Apply 1 layer 450g/m² CSM, using filled resin Day 7:

If a balsa or foam core is to be incorporated into the mould it should be left at this point for 7 days, at a temperature of 18°C to 23°C. This is to allow the mould to cure sufficiently before applying the core.

adhesive, and place primed balsa or punched PVC foam into the adhesive. Ideally, the core should be applied under vacuum, as it is vital that no air pockets remain to cause local delamination or blistering. Apply 1 layer 600g/m² CSM using filled resin. Allow to exotherm Apply 1 layer 600g/m² CSM using filled resin

The mould should be built up to the required thickness at a rate of not more than two layers 600 g/m^2 CSM per day, using filled resin. Care should be taken to ensure that the first layer has exothermed fully before applying the second layer.

Where a core is not being used, the mould should be built up under the same constraints of two layers $600g/m^2$ CSM per day, as outlined above.

Once the required thickness is achieved, the mould should be left for a minimum of 7 days before any backing structure is added.

To facilitate full cure, the mould should be post cured before releasing it from the plug, although this can sometimes be difficult. As plugs can be made from several disparate materials, movement and surface distortion can occur during post cure and this may lead to a distorted mould. Curing at even a modest temperature of 35° C to 50° C, however, is advantageous, as this will result in a mould with better temperature resistance. Where post curing is impossible, the completed mould should be left on the plug for at least two weeks at workshop temperature (18° C to 20° C).

Small imperfections in the surface of new FRP moulds can be removed using a fine abrasive such as metal polish or 600 grit wet emery paper, followed by a fine cutting compound and polish.

The correct storage and maintenance of a mould is important if it is to give long service. Any imperfections which arise during use should be rectified immediately. When not in use a mould should be stored flat on its base and protected from dirt and moisture.

HEALTH, SAFETY & THE ENVIRONMENT

Health and Safety

Any hazards associated with the handling of composite materials can be reduced to a minimum if the correct precautions are taken. Material Safety Data Sheets are available for all the materials mentioned in this handbook, and these should be read thoroughly before using specific products. General recommendations as to the storage and use of unsaturated polyester resins and their associated materials are contained in this section.

Storage

Liquid polyester resins are flammable. Most of the polyester resins in the Crystic range, for example, have a flashpoint of 32°C when tested in accordance with Schedule No.1 of the Highly Flammable Liquids and Liquified Petroleum Gases Regulations 1972 and are therefore subject to these regulations.

The storage (or shelf) life of polyester resins is three months for pre-accelerated systems, and 6 months for non-accelerated systems, provided that the resin is stored below 20°C in unopened containers. Storage at higher temperatures will considerably reduce the shelf life, as will storage in unsuitable containers such as glass. Tanks used for bulk storage of polyester resin should be inspected regularly and checked for contaminants. The formation of polystyrene can be reduced by the use of a wide bore vent (greater than 40mm) in the tank . The vent pipe should be accessible and as straight as is practical.

Accelerators and monomers such as styrene are also flammable, with flashpoints below 32°C, and have a shelf life of about 3 months at 20°C in suitable closed containers.

Most catalysts are organic peroxides and present a possible fire hazard. They should be stored in a separate area in a cool, well ventilated, fire resistant compartment. Users are advised to inform their local chief fire officer of the presence of organic peroxides on their premises.

Use

Most polyester resins contain monomeric styrene. Styrene is an effective grease solvent, so can cause drying of, and irritation to, the skin. Impervious gloves should therefore be worn when handling these materials. Any resin which does come into contact with the skin should be removed using a proprietary resin removing cream. Acetone or other solvents should NOT be used for this purpose. Taking these simple precautions will minimise any risk of skin irritation or dermatitis.

In sufficient concentration, styrene vapour is irritating to the eyes and respiratory passages. Workshops, therefore, must be well ventilated (see Quality Control Section). When resin is sprayed, a fresh air mask should be worn to protect the mouth and nose. This also applies to trimming operations when resin/glass dust can cause irritation.

Catalysts are extremely irritating to the skin and can cause burns if not washed off immediately with copious amounts of warm water. Particular care must be taken, when using liquid peroxide catalysts, to avoid splashing, spilling, or contact with the eyes. Protective safety glasses or goggles should be worn as a precaution when handling these materials. If organic peroxides do come into contact with the eyes, they can cause serious injury if not treated immediately. The affected eye should be washed with copious amounts of clean water for at least 15 minutes. Under no circumstances must the eye be treated with oily solutions, as these will aggravate the injury. **In all cases a Doctor should be consulted as soon as possible**.

Combustible materials such as cloths or paper, which have been contaminated with catalyst, can ignite spontaneously and should not be left lying in the open. A closed metal bin should be provided for such waste, and its contents should be safely disposed of, daily.

Resins, curing agents and most cleaning solvents are flammable and must be kept away from naked flames

or other sources of ignition.

If the precautions discussed in this section are followed, and a regime of good housekeeping adopted, polyester resins and their associated products can be used safely, and to best effect.

The Environment

Much work has been carried out over the past twenty years or so, to minimise the effect which materials such as those used in the production of composites, have on the environment.

The development of resins with low styrene emission properties was an early step in this process. These resin systems have reduced the levels of styrene to which operators, the workplace and the environment are exposed.

Polyester resins with a lower styrene content are now available from the Crystic range, and these have reduced even further the emission of styrene fumes to the atmosphere.

These resin systems, coupled with new processing techniques have made it possible for today's composites industry to produce high quality composite products whilst virtually eliminating polluting emissions.

Extensive research and development effort is being committed to minimising the impact that the composites industry of the 21st Century will have on the environment.

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International System of Units

Appendix 2

The International System of Units (SI), was introduced in 1960, by the General Conference of Weights and

Measures.

Relevant SI derived units

The system consists of base units, derived units and SI prefixes, and is now used all over the World.

SI Base Units		
Quantity	Name	Symbol
length	metre	m
mass	kilogram	kg
time	second	S
electrical current	ampere	А
thermodynamic temperature	kelvin	K
amount of substance	mole	mol
luminous intensity	candela	cd
specific heat	joules per kilogram kelvin	J/kgK
thermal conductivity	watts per metre kelvin	W/mK
thermal transmittance	watts per square metre kelvin	W/m ² K
temperature	degree kelvin	K
viscosity (dynamic)	pascal second	Pa s (=10 poise)

velocity	metres per second	m/s
frequency	hertz	Hz
force	Newton	Ν
stress, pressure	pascal, bar	Pa, bar (=105 Pa)
energy	joule	J
power	watt	W
impact strength	joules per square metre	J/m ²

Standard Prefixes		
Prefix	Symbol	Factor
tera	Т	10^{12}
giga	G	10 ⁹
mega	М	10^{6}
kilo	k	103
hecto	h	10^{2}_{1}
deca	da	10 ¹
deci	d	10 ⁻¹
centi	c	10 ⁻²
milli	m	10 ⁻³
micro	μ	10^{-6}
nano	n	10 ⁻⁹
pico	р	10^{-12}_{-15}
femto	f	10
atto	a	10 ⁻¹⁸

Scott Bader Product Range Resins, Reinforcements and Related Products

Crystic polyester resins

Crystic gelcoats Crystic epoxy resins Crystic epoxy curing agents Crystic pigment pastes Crestomer urethane acrylate resins Crestomer urethane acrylate adhesives West epoxy systems West & Senior pigment pastes

Scott Bader supply a comprehensive branded range of ancillary products

Reinforcements

Glass fibre chopped strand mats, rovings and surfacing tissues

Chomarat

Woven roving Rovimat glass fibre woven roving/chopped glass deposit combination Aramat Kevlar/glass fibre hybrid combination products. Kevlar fabric and carbon fibre fabric. Diagonap multi-axial reinforcements. Rovicore reinforcement for closed mould processes. Matline non-woven core material

C.S. Interglas

Glass fibre fabrics

Core Materials

Airex PVC foam sheet. Herex Scrim and Mini Scrim. Linear foam. Fire retardant (polyetherimide) foam.

Polyurethane foam

2 part polyurethane foam.. Polyurethane foam sheet.

Related Products

Scott Bader and Akzo Nobel catalysts Scott Bader and Akzo Nobel accelerators Araldite adhesives Frekote) Mirrorglaze) Release Agents Polywax) Sikaflex adhesive / sealant Swedtool laminating rollers

Our extensive range is continuously updated to meet the demands of the composites industry.

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