Unsaturated Polyester Resins

Polymers with unlimited possibilities

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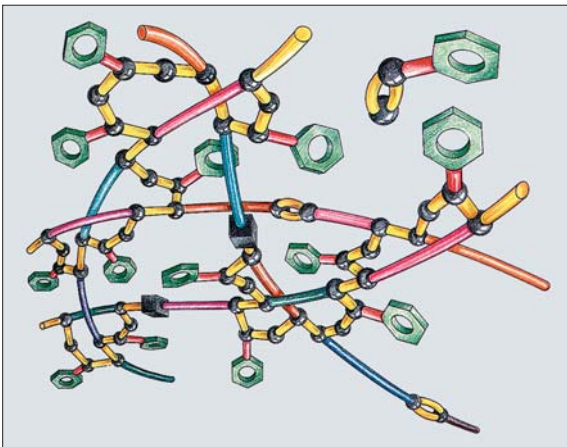
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The chemistry of unsaturated polyester resins

Introduction

Definition

An *unsaturated polyester* (UP) is a macro-molecule (average molecular weight between 1000 and 3000), built by a polycondensation reaction from dicarboxylic acids and di-alcohols. Some of the dicarboxylic acids contain carbon-carbon double bonds, so-called *unsaturated bonds*. At room temperature, the UP is a highly viscous liquid or a brittle glass-like product with a low melting point.

Reaction mechanism

An unsaturated polyester resin (UP resin) is a solution of the unsaturated polyester in a low-viscosity monomer, which also contains carbon-carbon double bonds. The most common monomer used is styrene. The carbon-carbon double bonds in the UP can react with the carbon-carbon double bonds in the monomer by means of a radical-initiated poly-merisation reaction. This process is called *curing* or *cross-linking*. The result is a three-dimensional (cross-linked) network. The product becomes a solid material, which no longer (contrary to thermoplastic polymers) melts during heating.

Components

There is a large variety of raw materials available for the production of UP resins. The choice of different dicarboxylic acids, di-alcohols and monomers results in a large range of products with a very wide spread of properties, which are suitable for many industrial applications, such as the boat building industry, the transport industry or building and corrosion resistant applications.

Formulation of standard resins

In the next paragraphs, the most commonly used raw materials for the production of UP resins are presented and the reaction mechanisms are described.

Raw materials

Unsaturated dicarboxylic acids
The essential feature of UP resins is the presence of carbon-carbon double bonds in the molecule. These double bonds are introduced through the unsaturated dicarboxylic acids. Although there are theoretically many possibilities, in practice the most commonly used unsaturated dicarboxylic acids are maleic anhydride, maleic acid and fumaric acid (Fig. 1). These acids render the best cross-linking possibilities with the styrene monomer (i.e. the possibility to form copolymers with styrene).

Saturated dicarboxylic acids
The degree of unsaturation is an important feature of UP resins. It influences the reactivity of the curing reaction and also the mechanical properties of the final product. A mixture of saturated and unsaturated dicarboxylic acids is normally used to adjust the degree of unsaturation. The most commonly used saturated dicarboxylic acids are orthophthalic acid, phthalic anhydride, isophthalic acid, terephthalic acid, adipic acid and hexachloro-endomethylene-tetrahydrophthalic acid (HET acid) (Fig. 2).
The choice of the saturated dicarboxylic acid also has an influence on the properties of the unsaturated polyester (such as the solubility in styrene) as well as on the properties of the final product (e.g. its corrosion
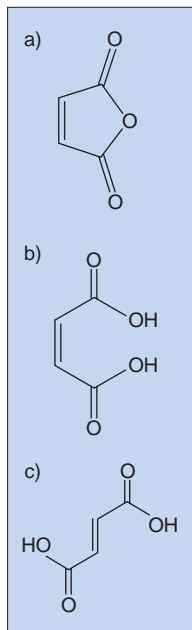
Fig. 1:
Unsaturated dicarboxylic acids for the production of unsaturated polyester resins
a) Maleic anhydride
b) Maleic acid
c) Fumaric acid
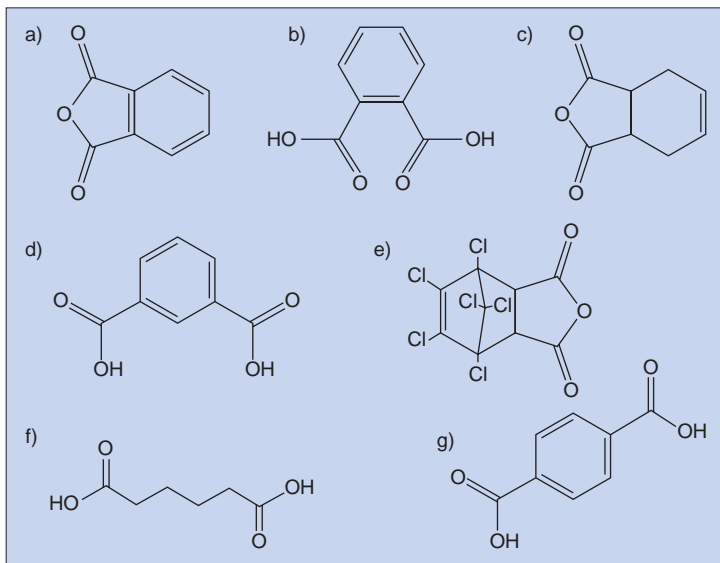
Fig. 2:
Saturated dicarb-
oxylic acids for the
production of un-
saturated polyester
resins
a) Phthalic anhydride
b) Orthophthalic acid
c) Tetrahydrophthalic
anhydride
d) Isophthalic acid
e) HET acid
anhydride
f) Adipic acid
g) Terephthalic acid

resistance and its mechanical properties).
Halogen-containing raw materials played an
important role in the production of flame-
retardant UP resins. They are still in use, but
are increasingly replaced nowadays by
halogen-free resin formulations, because
halogen compounds give off poisonous gases
in a fire situation.

Glycols

There is a wide range of glycols (bivalent
alcohols or di-alcohols) used in the production
of UP resins. The most commonly used are
diethylene glycol and dipropylene glycol. In
many formulations, mixtures of different di-
alcohols are used to obtain certain properties
of the final product. For more specific
applications, for example, those that demand
good resistance against chemical attack,
products such as neopentylglycol, 1,6-
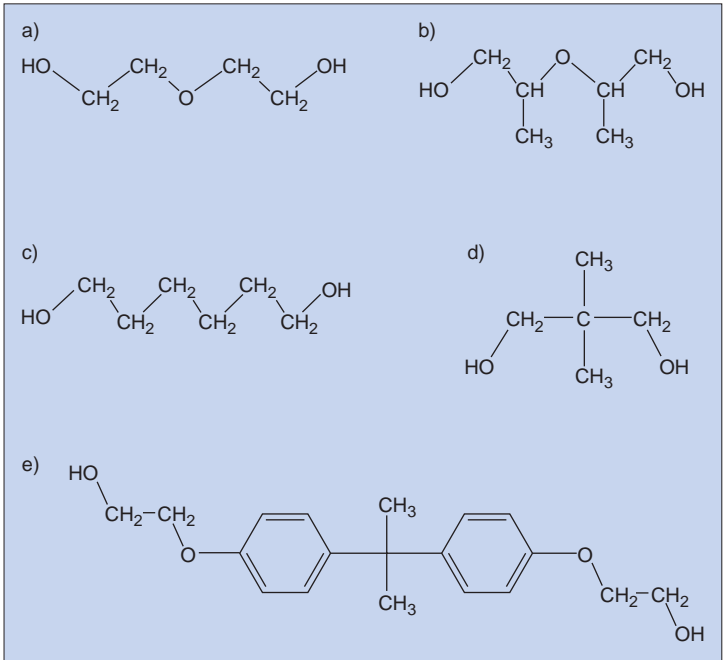
hexanediol and alkoxylated bisphenol A are used (Fig. 3).

Dicyclopentadiene
Dicyclopentadiene (DCPD) is a raw material which is formed as a by-product in the cracking of naphtha. It has been used for the synthesis of UP resins in the United States for many years and has now also found a growing interest in the European market. DCPD can give a number of specific properties to UP resins such as:

- increased heat resistance;
- less polymerisation shrinkage, which results in a better surface quality of the final product;

Fig. 3:
Glycols for the production of unsaturated polyester resins
a) Diethylene glycol
b) Dipropylene glycol
c) 1,6-Hexanediol
d) Neopentylglycol
e) Alkoxylated bisphenol A

• better wetting and impregnation of glass fibres.

There are two different ways to incorporate DCPD in a polymer backbone. In the first way, DCPD is reacted at 170 to 190°C by means of a retro-Diels-Alder reaction to form cyclopentadiene (CPD). The CPD then reacts immediately with maleic acid ester or fumaric acid ester to form the final polymer (Fig. 4).

Fig. 4:
The conversion of DCPD into CPD (top) and integration of the CPD into the polymer backbone by means of a reaction with maleic acid ester (bottom)

The second method to form DCPD resins is based on an addition reaction of unsaturated acids (such as maleic acid) to the ring of DCPD. This reaction runs at temperatures between 80 and 130°C. The formed half-ester reacts with the polyester chain and positions itself at the end of the chain. In this way, polymers with a low molecular weight are formed (Fig. 5).

Fig. 5:
Addition reaction between maleic acid and DCPD to form DCPD maleate
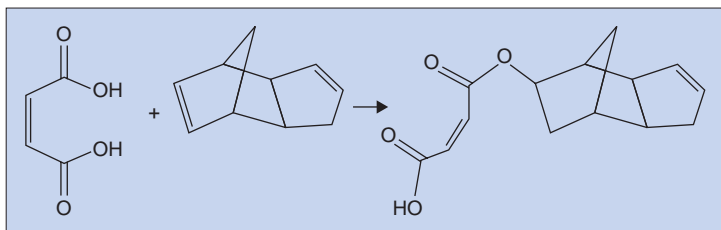
Reaction mechanism

UP resins are produced in two separate steps. In the first step, the unsaturated polyester is formed by the polycondensation reaction of the dicarboxylic acids and the glycols. In the second step, the UP is dissolved in the monomer and formulated to the final product.

In practice, all raw materials – propylene glycol, diethylene glycol, phthalic anhydride and maleic anhydride – are charged to the reactor. The volume of the reaction vessels is 20 to 25 m^3, but recently reaction vessels with a volume of about 55 m^3 have been installed. In order to avoid discoloration of the reaction product caused by the presence of oxygen, the air space in the reactor is flushed with nitrogen gas. The reactor content is then heated up to between 200 and 210°C (Fig. 6).

The polycondensation reaction starts during the heating-up phase, forming the polyester polymer under the separation of water. The water is distilled through a reflux cooler and condenser. The reaction is continued at 210°C

Polyconden-sation

Fig. 6:
Modern UP resin plant
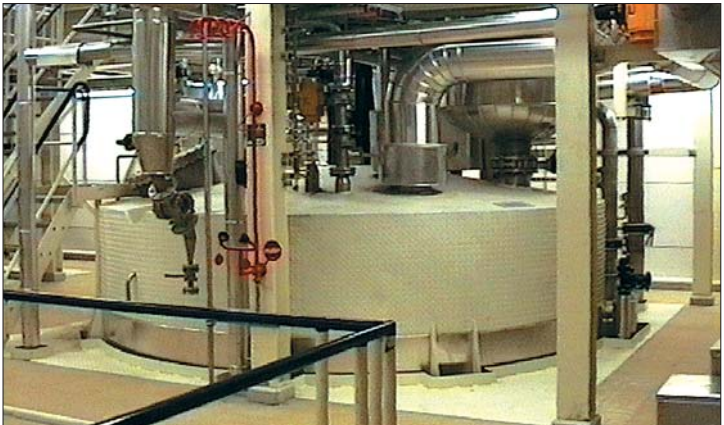
under the addition of nitrogen until the desired degree of polymerisation is obtained. At that moment, vacuum is applied to distil off the last traces of water. The polymer melt is then cooled down to between 60 and 80°C.

Dissolving the polymer melt

In the second step, the polymer melt is fed to a blender where it is dissolved in styrene monomer. Additives are added to obtain the required product properties such as reactivity, viscosity and shelf-life. The finished UP resin is filled into 200-kg steel drums, 1-ton containers or road tankers.

Formulation of vinyl ester resins

Raw materials

Vinyl ester resins are based on the reaction product of an epoxy resin with an unsaturated monocarboxylic acid. A specific feature in the molecule is the position of the carbon-carbon unsaturation, which is located at the end of the molecule.

The most commonly used epoxy resins are the diglycidylether of bisphenol A, the diglycidylether of tetrabromobisphenol A (Fig. 7) and the epoxidized phenol formaldehyde novolac. As the monocarboxylic acid, either acrylic acid or methacrylic acid is generally used.

Fig. 7:
Epoxy resin for the production of vinyl ester resins: diglycidylether of tetrabromobisphenol A
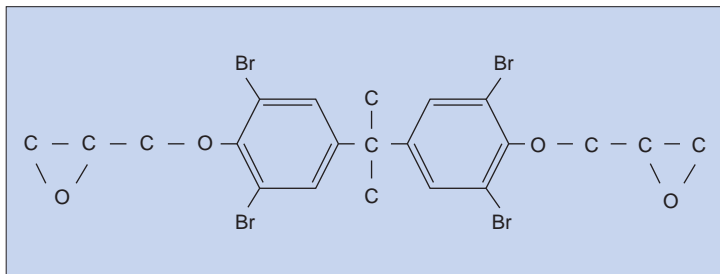
Reaction mechanism

The reaction between the epoxy resin and the carboxylic acid is an addition reaction which takes place at temperatures between 120 and 160°C. The addition of the carboxyl group to the epoxide ring results in the formation of an ester with a hydroxyl group (Fig. 8).

Addition reaction

The hydroxyl group can further react with anhydrides or isocyanates in order to obtain certain product properties in the final product. After the reaction, the vinyl ester is dissolved in a monomer (usually styrene) to form the final product.
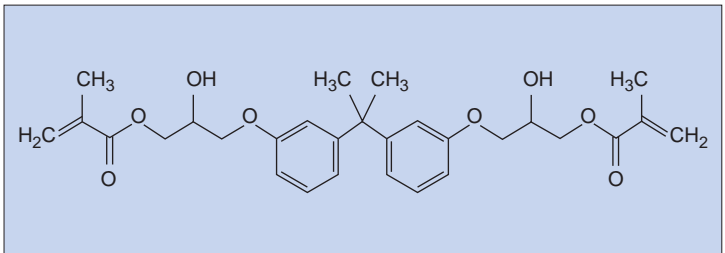
Vinyl ester resins combine the good thermal and mechanical properties of epoxy resins with the easier and quicker processing properties of unsaturated polyester resins. A specific property of vinyl ester resins is the resistance against a large number of chemicals. Vinyl ester resins are therefore used in the production of process equipment for chemical plants.

Fig. 8: Structure of vinyl ester

Specific properties

The curing of unsaturated polyester resins

As already mentioned, UP resins result from dissolving polycondensation products in a monomer. Both the polymer and the monomer

have reactive carbon-carbon double bonds. A reaction between these double bonds leads to the formation of a three-dimensional polymer network which serves to strengthen the product. This polymerisation reaction is irreversible: Once cured, the product cannot be re-melted. This is the difference between so-called thermoset plastics and thermoplastic polymers such as polyethylene, polyamide, etc.

Irreversible cross-linking

Monomers
In principle, all monomers which have a low viscosity and show sufficient reactivity in the cross-linking process can be used to dissolve UP resins and vinyl ester resins. In practice, other requirements are also important such as:

Fig. 9:
Monomers for the production of unsaturated polyester and vinyl ester resins
a) Styrene
b) Vinyl toluene
c) α-Methyl styrene
d) Methyl methacrylate

- low volatility;
- low, i.e. no toxicity;
- compatibility with the resin (good cross-linking possibilities);
- influence on the mechanical properties of the cured product;
- low price and high availability.
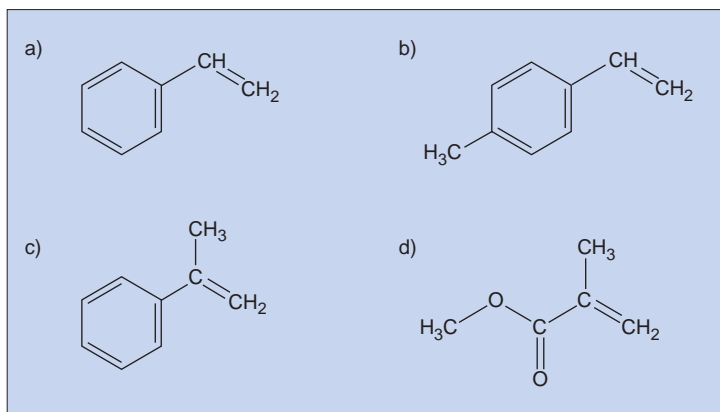
The most commonly used monomer is styrene, but methyl methacrylate, α-methyl styrene and vinyl toluene are also used, frequently in combination with styrene (Fig. 9).

The polymerisation process

The cross-linking reaction is a radical-initiated polymerisation reaction. Organic peroxides are used as radical initiators. There are many ways to process UP resins and each process has its own most appropriate organic peroxide. Radicals are generated by the decomposition of the organic peroxide. This is caused either by means of heat or by means of accelerators. The latter are frequently solutions of metal salts such as cobalt octoate with a concentration between 1 and 10% Co as the metal. The cobalt ions react with the organic peroxide in a redox reaction:

Radical-initiated reaction

$$ROOH + Co^{2+} \rightarrow RO^{\bullet} + Co^{3+} + OH^-$$
$$\underline{ROOH + Co^{3+} \rightarrow ROO^{\bullet} + Co^{2+} + H^+}$$
$$2\ ROOH \qquad \rightarrow RO^{\bullet} + ROO^{\bullet} + H_2O \quad +$$
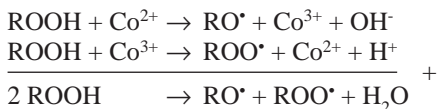
The curing reaction of UP resins at room temperature (cold curing) starts by adding the organic peroxide and the cobalt salt solution. Care must always be taken not to mix the peroxide and the cobalt solution in a pure form, as this will result in a violent decomposition reaction. Often, the manufacturer of the polyester resin already premixes the cobalt in the resin, so the reaction can be started by just adding the proper amount of peroxide. Methyl ethyl ketone peroxide is the organic peroxide that is by far the most-used one for cold curing processes (Fig. 10).

Cold curing

As soon as both components are added, radicals form which react with the carbon-carbon double bonds to form reactive places

Cross-linking and gelation
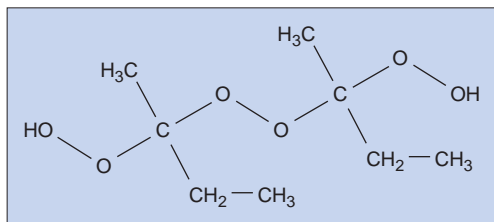
on the molecule. It takes some time before the polymer chains start to cross-link with the styrene molecules. In this phase, the product still remains liquid and can be processed in the proper way. As soon as the cross-linking reaction has progressed sufficiently, the resin forms a gel under the generation of heat. The choice of the curing system determines the speed of the reaction and the gel time. After gelation, the resin cannot be processed anymore.

Temperature development

The exothermic behaviour of the cross-linking reaction causes the temperature to increase, which further accelerates the polymerisation reaction. The gel solidifies progressively into a solid material. The temperature increases until a maximum is reached. From that moment on, the material cools down because the heat development is lower than the dissipation of the heat to the surroundings. The polymerisation reaction still proceeds, but this process slows down gradually until the final polymer network is formed. The material has solidified completely.

Process parameters

Factors that influence the curing reaction are the curing system used, the curing time as well as the temperature and the mass of material present during the reaction. The degree of curing is often determined by measuring the residual styrene monomer content in the final material. After the cross-linking reaction,

between 2 and 4% styrene monomer is generally still present in the product.

Styrene content

In many applications, lower residual styrene contents are necessary. For food applications, for example, it is very important that no residual products such as styrene leach out of the final product. Therefore the final product is often "post-cured" during a number of hours at elevated temperatures. This post-cure leads to a further cross-linking of the styrene monomer with the polymer backbone. Usually, a post-cure cycle takes 6 to 24 hours at temperatures between 60 and 100°C. Figure 11 gives a good overview of the relationship between the curing process, the temperature development and the residual styrene content.
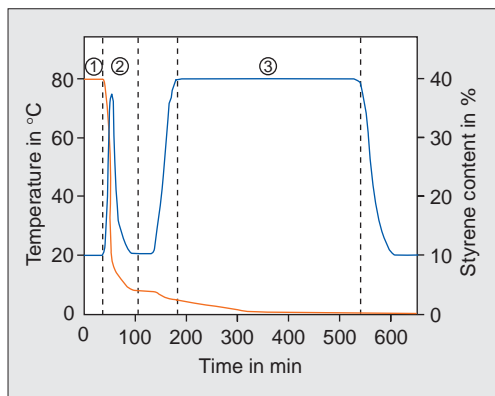
Fig. 11:
The curing reaction of unsaturated polyester resins
① Gel time
② Curing time
③ Post-curing
— Temperature
— Styrene content

Hot curing

Another way of curing the polyester resin is by using heat to decompose the organic peroxide. This is already possible at temperatures as low as 50°C, but in many cases temperatures of 120 to 160°C are used to generate sufficient radicals. Thereafter, the chemical reaction progresses in the same way as the described cold curing.
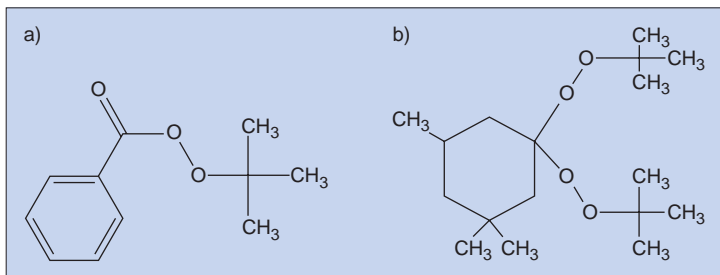
Fig. 12:
Organic peroxides used for high-temperature curing of UP resins
a) Tert. butyl perbenzoate
b) 1,1-Di-(tert. butyl peroxy)3,3,5-trimethyl cyclohexane

Suitable types of peroxides for this type of curing reaction are peresters such as tertiary butyl perbenzoate as well as perketals such as 1,1-di-(tert. butyl peroxy)3,3,5-trimethyl cyclohexane (Fig. 12). Mixtures of the UP resin with these peroxides show a long-term stability at room temperature.

Radical inhibitors

A radical polymerisation reaction can already start when a single radical is present in the material. Resins mixed with the peroxide and cobalt accelerators therefore show a limited stability. In some processes a longer working time is needed. This can be achieved by adding inhibitors to the mixture. These inhibitors can react with the free radicals at an early stage and render them inactive.

Increased working time

Certain inhibitors such as 4-tert. butyl catechol are used to increase the gel time of a mixture at room temperature, other types such as quinone-based compounds are used to increase the storage stability of the polyester resin.

Modifications of unsaturated polyester resins

Subsequent to the chemical synthesis of the unsaturated polyester and vinyl ester resins,

the properties of these base resins can be further improved by the addition of a variety of fillers and additives. As a result, resins are produced with processing properties which are adapted to the requirements of the process used by the customer. The customer does not have to add more components to the resin and can use the resin in the most optimal formulation. The upgrading process provides the base resins with specific processing properties and permits variation of the end-product properties (Fig. 13).

Additives and fillers
In the second production step, several additives and fillers are mixed or dispersed in the base resin. A mixing process is a simple agitation process used to mix in most of the additives. Some additives such as thixotropic agents, for example, have to be finely dispersed in the resin. This is

Mixing and dispersing processes

done with special high-speed dispersing equipment. The following sections describe the most important additives and their function.

Thixotropic agents

Thixotropy

Thixotropy is the property of a substance to change from a solid to a liquid state under stirring or shaking. Adding a thixotropic agent to a resin will decrease its viscosity, making it suitable for spray or hand laminating operations. As soon as the spray or hand laminating operation is finished and the resin is at rest again, its viscosity increases and as a consequence it will not sag from vertical or inclined surfaces. Pyrogenic silica is the most frequently used thixotropic agent.

Skin-forming additives

Reduced styrene emission

Skin-forming additives are used to prevent styrene emission from the resin during handling and curing. In many cases paraffin-based systems are used. Because the paraffin does not dissolve readily in the resin, a layer of the additive deposits on the surface of the resin as soon as the resin is no longer in motion. A skin forms relatively quickly which seals the surface and prevents emission.

Modern skin-forming additives are polymer-based and are also equipped with adhesion promoters. This prevents unwanted delaminating effects and guarantees optimal shear strength, even if the first layer of a laminate is already cured before the second layer is applied.

Viscosity modifiers

Styrene is the most important solvent and monomer for the manufacture of unsaturated polyester and vinyl ester resins, and is prob-

ably also the most well-known additive used to reduce the viscosity of resins. Methyl methacrylate and other acrylate and methacrylate monomers also serve this purpose. The advantage of these styrene-free solutions is that even though the content of styrene in the resin system does not increase, the desired effects, e.g. improved wetting of glass fibres and fillers, is still achieved.

Optimised viscosity

Fillers

Unsaturated polyester resins shrink when polymerising. Fillers can reduce this shrinkage. Chalk (calcium carbonate, $CaCO_3$) is a natural filler, available in abundant quantities, low in price and with a constant quality. It is the most-used filler in polyester resin applications. Other fillers that are regularly applied in polyester applications are sand, quartz, and slate flour. Of increasing importance is the use of finely ground waste from polyester production facilities or GRP (glass fibre-reinforced plastic) products. Fillers can constitute as much as 50% by weight of a GRP product.

Reduced shrinkage

Other fillers that serve a special purpose are, e.g. flame-retardant additives. Many applications in the building industry require fire retardancy. Polyester resins can be made fire retardant by adding antimony trioxide or halogen-containing compounds. Another very effective fire retardant is aluminium trihydrate ($Al(OH)_3$), added to resins for, e.g. the rail vehicle or building industry. This filler splits off water when heated above 200°C. This generation of water is strongly endothermic, so it has a cooling effect on a fire. Moreover, the water vapour acts as extinguishing agent and the formed aluminium oxide forms a protective skin on the burning surface.

Fire retardancy

Modified consistency

Magnesium oxide

Magnesium oxide (MgO) is an additive that thickens the resin and gives it a leathery consistency. This is why it is used above all in the manufacture of semi-finished products. Sheet moulding compound (SMC) is a semi-finished product which is finished in presses and therefore needs this highly viscous consistency.

Pigments and dyes

Pigments and dyes are used to give colour to polyester products. In some cases the pigments are mixed into the polyester resin in their pure form, very often however, the pigment is finely dispersed into a special, monomer-free polyes-

Fig. 14:
Filling station for colouring pastes

ter resin (see also chapter "Colouring pastes", p. 24). A colouring paste is obtained (Fig. 14) which is easier to handle and to dose to a resin. This makes it possible to give an opaque or also a transparent finish to gelcoats and resins in a number of different colour tones.

Protection against …

UV stabilisers

Polyester resins show some discoloration when exposed over years to direct sunlight.

The addition of UV stabilisers slows down this discoloration considerably. In the long term, however, the UV stabilisers are also decomposed by UV light and become inactive.

Speciality resins

Whether needed for hand-laminating, spray-up, vacuum or pressure injection, casting, filament winding or pressing operations, the proper choice of the base resin in combination with fillers and additives leads to virtually any desired processing property or product performance.

Environmentally friendly resins are formulated with lower quantities of styrene or by the addition of skin-forming additives. The already much lower styrene contents and the rapid floating of the skin-forming agents make it possible to reduce the emission of styrene by over 50%.

Examples

In addition, it is also possible to manufacture special resin systems such that the produced mouldings meet the fire safety regulation requirements. Resins developed especially for mould-making applications can also be produced from base resins. If resins are equipped with light initiators, they cure when exposed to UV light rays.

Gelcoats

Gelcoats are a particular, very important application of polyester resins. A gelcoat is the first layer that is applied on the mould surface and it will form the visual side of the final product after demoulding (Fig. 15). The gelcoat forms the visual appearance of the product, so the optical properties are very important. Even more, the weather resistance, fastness to light, gloss, chemical resistance and the mechanical properties of the

Functions

Fig. 15:
White gelcoat being sprayed onto a boat mould

surface are decisive for the quality of the product.

The possibilities to supply gelcoats in different colours are unlimited. With modern colouring technologies, any colour can be made reproducibly to colour specification, whereby the actual colouring process is usually done by the manufacturer direct.

Gelcoats usually already contain the required amount of accelerator (mostly cobalt salt solution). This "pre-acceleration" is necessary to start curing at room temperature. If the proper amount of curing agent is added to the mixture and the instructions of the manufacturer are observed, good results are guaranteed.

Application   Gelcoats are applied manually with a brush or a roller, or by spraying with spray guns. Gelcoats are normally applied in relatively thin layers of around 500 to 600 µm (this corresponds to approx. 0.6 to 0.7 kg of gelcoat per m^2). They are adjusted to a high thixotropy in order to prevent any sagging

from vertical surfaces. In the development of gelcoats, much attention is paid to good processing properties, de-aeration possibilities and wetting of the mould surface. Especially important is the careful handling of the gelcoat.

Bonding pastes and repair putties

Similar to the gelcoats, bonding pastes and repair putties are also produced with high-speed dispersion processes. In the modern adhesive and bonding industry, a large number of products are sold in

Manufacture and processing

Fig. 16:
Manual application of a bonding paste

many different markets. The use of high concentrations of fillers in the formulations compensates the polymerisation shrinkage of UP resins in adhesive pastes. Bonding pastes are applied to the substrates manually or by means of dosing equipment (Fig. 16).

Apart from structure and material of the substrate, the demands on the finished product are decisive for the choice of the resin or the formulation of the bonding paste. As bonding pastes used in the boat building industry must be able to absorb high shear forces, they often contain glass fibres as a

Demands and utilization

filler. In lightweight construction applications (e.g. sandwich constructions), bonding pastes with low-density fillers are used, while elastified, high-temperature or corrosion-resistant products are used for the production of storage tanks and chemical plants. Large amounts of bonding pastes are used in the production of windmill rotor blades. They must have very good fatigue properties, which is why vinyl ester resins are used as the base resin.

Repair putties are used in the car repair industry or to smooth laminate surface structures in the boat building industry. The resin used in car repair putties must show an excellent adhesion to various substrates such as steel, galvanised steel and plastics, e.g. ABS and polypropylene.

Colouring pastes

Production   Colouring pastes are produced by milling pigments into a monomer-free polyester resin. Pearl mills or roller mills are used to ensure the finest possible dispersion of the pigment. For some pigments, this milling operation can take several days.

Applications   Colouring pastes can be used for the direct colouring of laminates. In this case, an addition of 3 to 5% to a laminating resin is sufficient. How much is used depends on the desired colour tone, the application, and the recommendations of the manufacturer. In the same way as with paint, these pastes are capable of covering the entire colour spectrum. The biggest application for colouring pastes is, however, for the production of gelcoats. A gelcoat of a certain colour is formulated with a combination of several base colours. Colour measuring equipment is used to determine the exact colour and for colour matching.

Colour determination
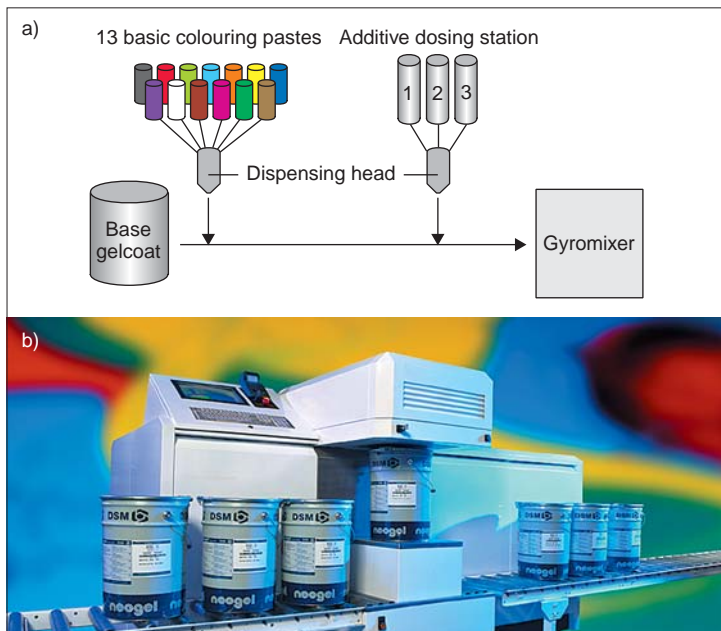
The use of modern "tinting systems" has led to a high flexibility in the production of gelcoats of any colour. Many thousands of colours are programmed in a tinting machine. The system delivers the exact required quantities of a fixed number of colouring pastes into a clear or white base gelcoat. The tinting technology is known from the paint industry, but has to be adapted specifically for the polyester industry due to the high viscosity of the colouring pastes and the gelcoats. Once adapted, however, even mini batches of coloured gelcoats of constant quality can be produced and delivered (Fig. 17).

Fig. 17:
Tinting system
a) Schematic of
*   the function*
b) Eurotinter

Properties of resins and composites

UP resins are very often used as construction material in combination with reinforcing fibres. Glass fibres are the most commonly used reinforcing fibres (GRP: glass fibre-reinforced plastic). There is a growth in the application of carbon fibres as reinforcement, but for cost reasons their use is restricted to specialised and highly demanding applications.

Composites: Structure …

Combinations of reinforcing fibres and a resinous matrix are referred to as composite materials or "composites". Composites are basically inhomogeneous and anisotropic materials: The properties differ from place to place in the material and differ also in different directions. In composites, the good properties of the reinforcing fibres (strength, stiffness) are combined with the good properties of the resin (protection against moisture, corrosion resistance, etc.). Compared to the usual construction materials such as steel, concrete, wood and aluminium, composites have a number of unique material properties. These properties are caused partly by the material itself and partly by the processing methods used in the production of the composite materials.

… and properties

In the next section, a number of material properties are explained and the differences between composite materials and the usual construction materials steel and aluminium are given.

Weight

Steel has a specific weight of 7.8 kg/dm^3, aluminium of 2.7 kg/dm^3 and composites of

approx. 2.2 kg/dm^3. On a volume basis, composites have the lowest weight. However, weight alone is not always the decisive factor when choosing a construction material; the mechanical properties are also of great importance.

Strength

The dimensions of most materials change under load. In comparing different materials under load, stiffness is measured. The degree of stiffness is expressed as the modulus of elasticity, abbreviated to the E-modulus. Steel, for example, has an E-modulus of approx. 210,000 MPa, whereas composites have an E-modulus of between 7000 and 40,000 MPa, depending on the glass content and glass fibre orientation in the composite.

Table 1:
Mechanical properties of composites, compared with steel, aluminium and wood

	Unit	Non-reinforced UP resin	GRP with chopped strand mat	GRP with bidirectional roving fabric	GRP with unidirectional roving fabric	Construction steel	Aluminium	Wood
Glass content	% by weight	–	30 – 35	60	75	–	–	
Tensile strength	MPa	75	120	350	1200	390	250	100 – 180
E-modulus	MPa	3300	8500	20,000	40,000	210,000	80,000	8000 – 15,000
Flexural strength	MPa	130	245	360	1 200	430	330	70 – 140
Density	kg/m^3	1300	1450	1750	2000	7800	2700	600 – 1100
Strength per weight unit	MPa/ kg	1.1	1.7	4	12	1	1.87	3.3

The combination of mechanical properties and weight gives an interesting comparison between metals and composites. If the mechanical properties are compared as a function of the specific weight in each case, composites prove to be really lightweight construction materials (Table 1).

Electrical properties

Electrical insulators

Composites are electrical insulators. They can therefore be used in many electrical applications where metals cannot. Examples are electrical switchboxes, ladders and cable gutters.

Thermal properties

Thermoset polymers

Unsaturated polyester resins are thermoset polymers. They cannot be made liquid again by increasing the temperature, as can thermoplastic polymers (polyethylene, polyamide, etc.). The polymerisation reaction is irreversible.

In spite of this, when UP resins are exposed to higher temperatures, they become more flexible. The mechanical properties change. It is therefore important to know at which temperatures composite materials can still be used. The "heat deflection temperature" (HDT; ISO 75) is an indication for the maximum temperature that can be applied to composite materials. For standard polyester resins, the HDT ranges between 60 and 100°C.

Long-term heat resistance

The long-term heat resistance is another important property of composites. When exposed to high temperatures for a longer period, UP resins slowly degrade and show a number of changes. Most important are the increase of stiffness (caused by continued cross-linking), the lowering of strength

(caused by increased brittleness) and the change of appearance (discoloration, crack formation, etc.) caused by oxidation processes. Composites made with standard UP resins can withstand long-term exposure to temperatures up to between 80 and 120°C. The use of special heat-resistant UP resins makes long-term exposure to temperatures as high as 220°C possible.

Special heat-resistant resins

Corrosion properties

UP resins show very good corrosion behaviour. The use of standard UP resins is

*Fig. 18:
Chlorine filtration plant*

very widespread in boat building. Boats built 40 years ago still show a very good resistance against the continuous exposure to water.

High corrosion resistance When more demanding corrosion resistance is required, a whole range of different resin formulations is available. The highest corrosion resistance is obtained with bisphenol-A-based resins and vinyl ester resins. Typical applications for vinyl ester resins are storage tanks for strong acids, solvents, mineral oils, etc. Vinyl ester resins also show good thermal stability. They are therefore also used in high-temperature applications such as chimneys, chlorine filtration plants, etc. (Fig. 18).

Processing techniques

Just as wide as the range of UP resins and their formulations is the range of different processing techniques, from manual operations to highly industrialised processes. The choice of the processing technique depends on many factors such as the size and the complexity of the product and the production numbers.

Two ways of processing must be distinguished, i.e. open-mould processes and closed-mould processes. In open-mould processing, a single mould is used in which the product is made. The mould is a negative form of the final product, usually a female mould. In contrast, closed moulds are made up of two parts. The surface condition of the mould largely influences the quality of the final product. The production of a good-quality mould is no quick and easy matter.

Open- and closed-mould processing

Mould making

Moulds for open-mould processes are frequently made out of glass fibre-reinforced vinyl ester or epoxy resins. Compared to metal moulds, the advantages of these composite moulds are:

Alternative to metal moulds

- they are relatively cheap to produce and easy to manufacture;
- they are suitable for the production of large products;
- repairs and modifications can be easily done.

Composite moulds also have some disadvantages:

- they have a relatively short production life, i.e. the number of products that can be made with composite moulds is limited;
- the surface quality is generally not as good as with metal moulds;
- the strength of composites limits their use in closed-mould applications.

Work cycle: Production of the master pattern

GRP (glass fiber-reinforced plastic) moulds are made as follows: As a first step, a model or master pattern is made from wood, plaster, steel, plastic, etc. The master pattern is a replica of the finished product. The master must have a high-quality surface finish, because the production moulds are made from it. The next step is to produce a master mould or production mould from the master pattern. The following general points must always be considered:

- The surface finish of the master pattern dictates the quality of the surface finish of the final product.
- Good mould making is a slow and careful process. Attempts to use shortcuts usually lead to inferior products.

A surface coating or wax must be applied to the master pattern to act as a barrier and release agent between the pattern and the mould.

Lamination

A layer of dark-coloured gelcoat is then applied to the pattern. After sufficient curing of the gelcoat layer, the lamination can start. A layer of catalysed resin is applied to the gelcoat and a glass fibre surface tissue is brushed carefully into the resin. The surface tissue prevents any glass fibre pattern showing through the gelcoat and minimises the risk of air entrapment immediately behind the gelcoat. When the surface tissue layer is sufficiently cured, lamination can continue. Layers of

chopped strand mat are applied together with catalysed resin. Sufficient layers have to be applied in order to impart the required strength and stiffness to the mould.

When all laminating work is done, the mould is cured, still on the pattern, for at least 48 hours at room temperature. Reinforcing ribs and supports, etc. are then positioned at the relevant locations. The mould is then post-cured during 6 to 8 hours at 50 to 60°C before it can be released carefully from the pattern.

Curing

Before the mould is used for production of the final products, it must be impregnated with release wax in order to protect the surface from attack by styrene monomer.

Surface processing

Hand lay-up technique

Even though the hand lay-up technique is the oldest of the processes for glass fibre-reinforced plastics, it is still used today for the production of medium- to large-size products in limited piece numbers such as covers for machines and installations, boat hulls and

Applications
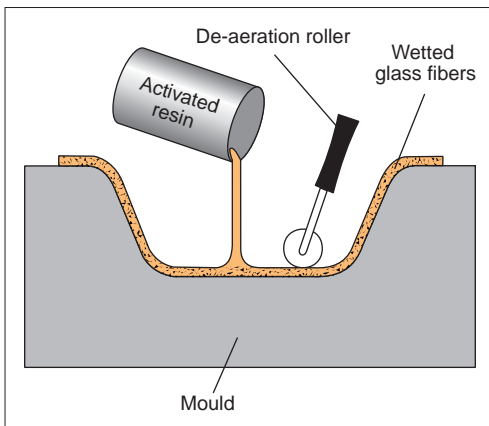
Fig. 19: Hand lay-up

Characteristics   decks, trailers, etc. (Fig. 19). The hand lay-up technique is also a very important processing technique extensively used for mould making, prototyping and development purposes (Fig. 20).

Because the final result depends directly on the skills of the operator, well-trained operators are a prerequisite. Operator costs constitute a large part of the total costs of this processing technique.

Fig. 20:
Manufacture of
a boat hull using
the hand lay-up
technique

Process steps

Before starting the lamination, the mould is cleaned carefully and release agent is applied to the mould. Subsequently the gelcoat, if required, is applied. Then layers of glass mat are cut to the required shape, put into place in the open mould and saturated with polyester resin. The glass fibres must be completely wetted out by the resin and air bubbles must be removed with special serrated rollers. After curing at room temperature, the mouldings are

removed from the mould, trimmed and finished.

Spray-up technique

Spray-up is a partly mechanised version of the hand lay-up process. The resin is applied to the mould surface simultaneously with chopped glass fibre rovings (Fig. 21).

Fig. 21:
Spray-up

Procedure
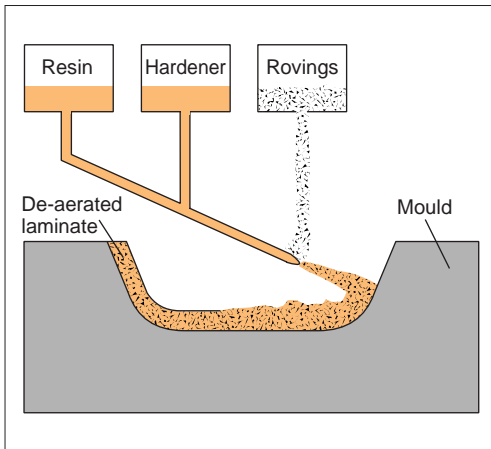
In the spray gun, the resin is premixed with the organic peroxide. At the same time, the glass fibres are pulled from a roving spool and fed into rolling knives (cutters) by means of air pressure. They are cut into lengths varying from 20 to 60 mm. The glass fibres are blown into the resin spray and are deposited on the mould surface together with the resin. Similar to the hand lay-up process, it is also necessary here to impregnate the glass fibres, which is done with brushes and rollers, and to remove enclosed air bubbles with special serrated rollers.

Variants   In the conventional spray-up process, a certain amount of styrene evaporates. New spray equipment nowadays operates with sophisticated methods to spray the resin without forming a mist of small particles. Specially shaped nozzles or fluid impingement techniques are used to reduce the evaporation surface area of the resin droplets. A considerable reduction in the styrene emission is the result. In combination with the use of resins with a lower styrene content and skin-forming additives, this modern equipment has succeeded in reducing the exposure of workers to styrene considerably.

Applications The spray-up technique is particularly suitable for the production of parts with complicated contours. When made with the hand lay-up technique, a lot of parts have to be cut from the glass fibre mats. This is a labour-intensive operation and leads also to considerable loss of material. The glass fibre material for spray-up is used in the form of a continuous roving, which is the cheapest available form of glass fibre.

With spray-up, the quality of the final products also depends – in a similar way to the hand lay-up technique – on the skills of the operator. Whereas the use of cut mats guarantees a constant glass content, even over large surfaces, fibre-sprayed parts often have varying wall thicknesses with varying glass content.

Injection processes

Injection processes, also known as resin transfer moulding (RTM) processes, are by no means new. There are several variations possible for injection processes, but they are all based on the same principle, i.e. a

resin, already equipped with the proper curing system, is injected into a closed, double-sided mould. This can be done under high pressures (up to 20 bar), but also under vacuum.

The process starts by cutting the reinforcing material in the appropriate shape of the final product. This is then placed in the mould. Alternatively, prefabricated reinforcements called preforms are used. Together with the reinforcements, other products such as PU or PVC foam and metal inserts are placed in the mould. In this way, parts that are important for the later function of the moulding (e.g. metal threads for bolted connections) are integrated at an early stage.

Double-sided moulds are now closed. For very large structures, which are made by vacuum injection (e.g. boats, windmills, etc.), a flexible film is used as the upper mould. The film is draped on top of the reinforcement. As soon as the vacuum is applied, the film is drawn into the mould and will follow the contours of the product. Then a carefully

Work cycle
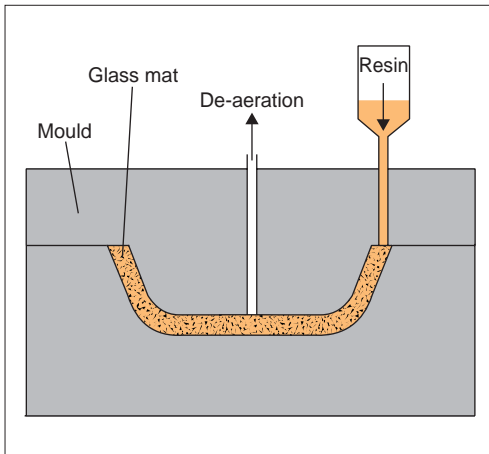
Fig. 22:
Injection process

calculated amount of activated resin is injected. After curing, the film or the upper mould is removed and the product is taken out of the mould.

Advantages   Important advantages of this closed-mould system are the absence of styrene emission, a high reproducibility and a far less labour-intensive operation. With injection processes, products of a high quality can be produced.

Filament winding

Principle   The filament winding process differs from the foregoing processes in that the reinforcing fibres are wound onto a positive mandrel. Filament winding is a process to produce hollow, cylindrical, oval, conical or spherical shapes in GRP. The most important applications for this process are tanks, containers, silos (on which the end caps are frequently hand-laminated), and pipes.

Process variants   There are various ways to produce filament-wound articles. A distinction can be made between the winding principles (lathe winding, wobble winding or planetary winding), the reinforcing material (stripe winding, roving and filament winding) and also between the angle of the reinforcement to the winding axis (biaxial winding, parallel winding or cross winding).

The reinforcement is drawn through an impregnating bath, which contains the resin, already equipped with the proper curing system. Depending on the application the resin may also contain fillers. The reinforcement is wound on a rotating mandrel until the required wall thickness is reached (Fig. 23). The winding angle and the glass content can be adjusted to obtain the required mechanical properties.
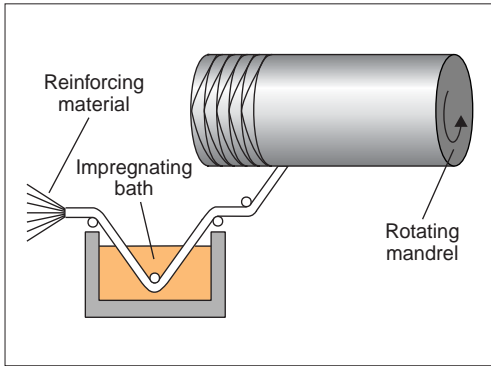
Typically, cylinder diameters ranging from 40 mm to 8 m are wound on stationary machines (i.e. in a factory). For bigger diameters (which will present a transport problem), winding machines have been developed with which a product can be produced directly on site.

For the industrial production of pipes in large lengths, a continuous winding process, the Drostholm process, has been developed. In this process the winding mandrel is an endless stainless steel band which runs under an angle on a turning support construction. Set into rotation, the band makes a helical movement and the webs of resin-impregnated reinforcing material are continuously wound. The complete mass goes through a ring oven in which the curing takes place. After the curing oven, the steel band is released from the inside and moved back to the start of the process. The cured wound part is transported to a cutting system and cut into pieces.

Drostholm process

Centrifugal casting

Centrifugal casting is an industrial process for the production of pipes, masts (e.g. flagpoles),

Equipment

rollers and containers. The casting equipment consists of a cylinder (often made of steel), which lays on a series of bearings and can rotate with adjustable speed. The drive is via either V-belts or rollers, upon which the cylinder rests.

Very often, a mixture of glass fibres and resin is dosed simultaneously to the rotating cylinder (Fig. 24). As a result of the centrifugal forces, the glass fibres are impregnated and optimally de-aerated. A tube with a good surface quality is the result.

The mechanical properties of the tubes are determined by the amount of reinforcing fibres as well as by the turning speed of the cylinder.

Fig. 24:
Centrifugal casting
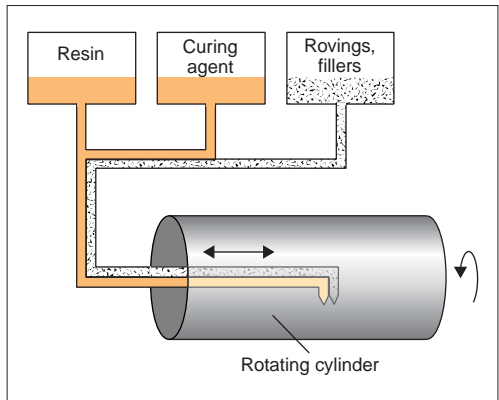
Characteristics

Tubes which are used for sewage water transport must have a high wall thickness, resulting in a good cylindrical stiffness. For this purpose, sand is added to the resin/glass fibre mixture, which increases the total mass of the pipe.

Considering the (low) amount of work involved, the centrifugal casting process is extremely rational. Notwithstanding this, relatively expensive centrifugal cylinders and

precisely balanced units are necessary. Because of this, the process is only of interest for series manufacture.

Another application of the casting process, where no fibre reinforcement is used, is the production of buttons. In this case, the activated resin is poured into a rotating cylinder. The curing system is adjusted in such way that a slow and gradual cure develops. Before curing is complete, the still flexible sheet of resin is taken from the cylinder and rolled out. Button rounds can be punched from the sheet and subsequently cured in hot water.

Applications

Casting

Another process for the application of UP resins without using reinforcing fibres is the casting process. The activated resin is cast manually or by means of a dosing machine in a hollow mould where it cures and solidifies. In many cases the resins are mixed

Manual or machine processing
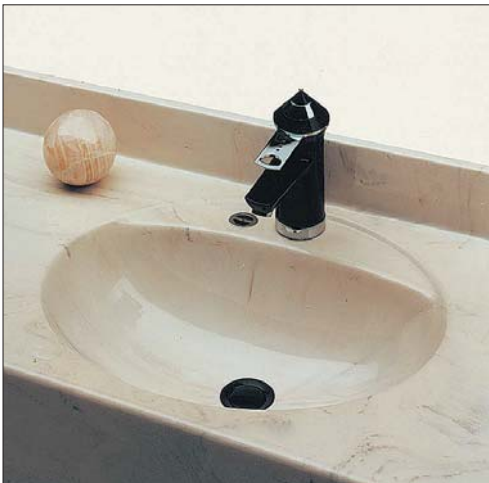
Fig. 25: Washbasin manufactured using the casting technique

with fillers to obtain less shrinkage during cure or to save costs on raw materials. The fillers can also have a functional effect such as giving colour or hardness to the cast article. In some cases the mould is coated with a gelcoat beforehand or the resin is coloured with a colouring paste.

The casting process is used for the production of sanitary articles (e.g. kitchen sinks or washbasins, Fig. 25), marking stones, drain gutters, cattle feeding troughs, furniture ornaments or rods for the production of buttons.

Pultrusion

Pultrusion is a technique to produce glass fibre-reinforced profiles. Dry glass fibre rovings are pulled through a resin bath in which they are impregnated with UP resin. After impregnation, the fibres are pulled through a heated die in which the resin cures at temperatures of 110 to 160°C. The die has the shape of the end product. After curing in the die, the profiles are cooled down and cut to the desired length.
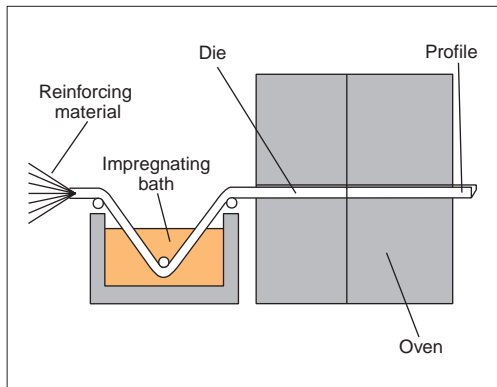
Fig. 26:
Pultrusion

With the pultrusion process, virtually every desired profile can be manufactured. A wide range of standard industrial profiles is available in the usual U-, I- and O-shapes, but with pultrusion, very complicated profiles can also be made. These profiles find their use in a wide variety of end markets.

Advantages of the process …

Early applications for pultruded profiles were the production of fishing rods. Nowadays, they are used, e.g. in the transport sector, for infrastructural applications and in the chemical industry for walking grids.

Pultruded profiles have a high glass fibre content and consequently a very high mechanical rigidity. This is a particular advantage in civil engineering applications such as bridge-building and constructions for production installations. Compared to steel profiles, GRP-pultruded profiles show a much better corrosion resistance and have better electrical insulating properties.

… and the products

Pressing processes

Pressing processes are used for the production of complicated shapes with a high reproducibility. These processes are typically suited for large-series production.

There are two distinctly different pressing processes, i.e. wet pressing and hot press moulding using a semi-finished intermediate such as SMC (sheet moulding compound) or BMC (bulk moulding compound).

Suitable for repetitive work

Wet pressing

In the wet pressing process, the reinforcing materials – cut-to-size glass mats, woven glass or preshaped glass mats (also called preforms) – are placed dry in the mould. The mould is always a double mould, made of UP or

epoxy resin or of metal, fixed in a hydraulic press.

Cold pressing

A carefully metered quantity of resin that contains all the necessary fillers, pigments and curing agents, is poured on top of the reinforcement and the mould is closed. In general, high-reactive resins are used in this process. As a result of the polymerisation heat, the mould heats to a temperature of 40 to 70°C. This accelerates the curing process even more. When the process is running well, an equilibrium is formed between the heat generated by the polymerisation and the heat dissipated to the surroundings. Once this point has been achieved, four to eight products can be produced per hour.

Warm pressing

When heatable steel moulds are used, the cycle time can be further reduced. The process is then called warm pressing. Heating of the moulds can be done with steam, heating oil or electricity. A temperature of 80 to 140°C is reached. Just as with cold pressing, the mould is charged with reinforcing

Fig. 27:
Wet pressing
production

material and in many cases with an already activated resin mass that contains fillers. The mould closing speed is slowed down in the last stage of closing. This prevents any movement of the reinforcement due to a high resin flow, and gives the air an opportunity to escape from the glass reinforcement. Depending on the resin type, the wall thickness and the temperature, a cycle time of 3 to 5 min can be reached. Warm pressing is a very economic process, suitable for the production of larger series in a good quality that is free from entrapped air (Fig. 27).

Processing of moulding compounds

A breakthrough in the industrial-scale manu-facture of products for the electric and the automotive industry was reached by using moulding compounds in a pressing process. The typical composition of the SMC and BMC materials processed in this way is shown in Table 2.

Semi-finished products SMC and BMC

Raw material		SMC	BMC
UP resin		50 – 70	50 – 70
Low-profile additive (LPA)		30 – 50	30 – 50*⁾
Organic peroxide (phr)		1.0 – 2.0	1.0 – 2.0
Fillers (phr)		100 – 200	175 – 350
Zinc stearate (phr)		3.0 – 6.0	2.0 – 5.0
Pigments (phr)		0 – 10	0 – 10
Magnesium oxide paste (35% MgO, phr)		1.0 – 2.0	0.3 – 2.0
Glass fibre	Fibre length (mm)	20 – 50	3 – 12
	Glass fibre content	20 – 40	3 – 15

*Table 2: Typical composition of SMC and BMC (phr: per hundred parts of resin + LPA; *⁾: resin + LPA = 100)*

Sheet moulding compound

The use of sheet moulding compound is a very important production process for the production of GRP parts. SMC is a flat sheet-like compound, produced in a continuous moving belt process and coated on both sides with polyethylene or polyamide film.

Components As glass fibre reinforcement, cut glass rovings are used in most cases. Calcium carbonate is the most commonly used filler. Because resin and glass – the major components – are available in many different variations and can be combined at will, the respective product can be tailored to the individual requirements (e.g. weather-resistance, resistance to chemical attack, high surface quality, mechanical strength) in an optimal manner.

Additives Magnesium oxide in the formulation can react with the free acid groups of the resin. This results after a few days in an enormous increase of the viscosity of the SMC formulation. A leather-like sheet is formed which is almost non-sticky and easy to handle – a prerequisite not only for the robot-controlled cutting to shape, but also for the entire automatic treatment process. The resin

Fig. 28:
SMC is used, e.g. for the production of car boot lids
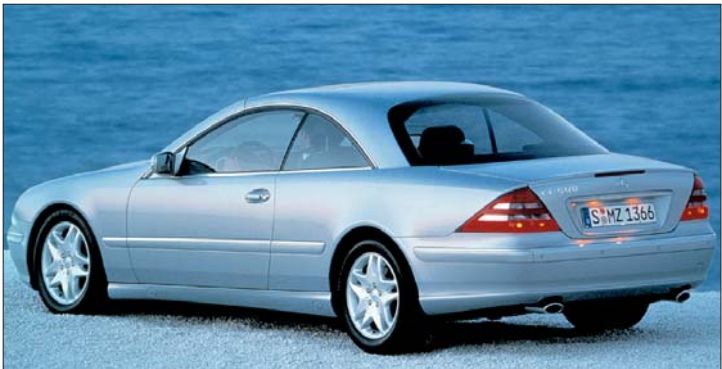
is still not polymerised at this point, and cross-linking does not occur until after moulding. The accelerator and all other additives necessary for the process are, however, already contained in the semi-finished product.

Processing

The protective polyamide film is removed from the pieces, which are then placed into the steel mould. The mould is closed and at a pressure of 100 bar and a temperature of 150°C, the SMC flows into the mould cavities where it cures. The cycle time for an SMC press operation is – depending on the size and complexity of the product – between 30 s and 3 min.

In the production of car body parts, SMC systems have been developed that cure without shrinkage (Fig. 28). The result is a high-quality surface of the parts, a so-called "class A" surface. This quality is equivalent to a "mirror-like" finish.

Production plant

SMC production installations represent the state of the art. Most of the process parameters such as weight per area unit, glass content and filler content are programmable. A microprocessor controls the machine parameters such as the feed rate, belt speed or speed of the cutting unit. During production operations, these data are monitored constantly.

Bulk moulding compound

For the production of certain complex parts, the use of bulk moulding compound is a variation on the SMC technology.

BMC is a dough-like material, made by mixing all ingredients together in a heavy-duty mixer. BMC is usually processed by means of injection moulding or compression moulding. A typical product made of BMC is a headlamp reflector (Fig. 29). These are injection-moulded fully automatically in very

*Fig. 29:
Headlamp with a
reflector made of
BMC*

short cycle times. Modern installations produce several thousands of these products per day.

Applications of unsaturated polyester resins

Boat building

The marine industry is a classic example of an application for glass fibre-reinforced UP resins. Around the 1950s, the first small rowing, sailing and motorboats were produced in series from standard orthophthalic resins. In an area where a lot of parts were made by hand, GRP showed a tremendous potential as a new construction material for the production of complete ship hulls and decks in series production. It revolutionised the ship building industry.

Today, the marine industry is still a major application area for glass fibre-reinforced UP resins (Fig. 30). To an increasing extent, boats, yachts and motorboats are being made of these resins. Convincing is not only their impressive

Classic applications

Fig. 30: Boat building is an important application area for glass fibre-reinforced plastics

properties but also a favourable price-per-formance ratio.

Building industry

Flat and corrugated sheets, light domes and skylights, rain gutters, complete covers for sewage water treatment plants, washbasins, shower cabins, dormer windows and door ornaments – this list of products, which can be

Fig. 31:
Rain gutter made
of GRP

easily extended to a great length, shows the versatility of the use of GRP as a construction material in the building industry (Figs. 31 and 32).

Advantages of the material

The strong points of GRP in this market are the freedom of design, a high dimensional accuracy of the product as well as the excellent compatibility with other construction materials.

In chemical plants, the construction materials must be able to withstand harsh conditions such as exposure to water, acids and solvents, oxidising media and changing temperature conditions. There is hardly a material that is better suited for these conditions than glass fibre-reinforced UP resins.

New areas in civil engineering where the use of GRP shows potential is in the construction of bridges and concrete repair.

Fig. 32:
GRP is also used for the construction of swimming pools

Transport industry

The material properties of composites make these materials very suitable for applications in the car and lorry industry. GRP parts for industrial and utility vehicles (e.g. machine covers, spoilers, roof sleepers, side skirts, etc.) were among the first to be made in series production. Car body parts for passenger cars were first made in small series. Around 1970, GRP started to be used for car bumpers. The further development of resins and systems for SMC and BMC made it possible to produce high-quality class A products in very large series. Nowadays, many car brands apply GRP in the production of engine covers, door elements, boot lids, etc. Some cars even have complete GRP bodies.

Production of vehicle components

Manufacture of complete car bodies

Today, the potential for GRP is not by far fully explored. New applications come on the market regularly, especially in public transport (light-rail systems, high-speed trains), the aircraft industry and in the production of leisure vehicles such as caravans and mobile homes. Here again, the use of GRP is based on a number of sound arguments:

• Compared with steel, GRP parts are approx. 40% lighter at the same stiffness. This leads to a substantial reduction of weight and thus a better fuel economy (Fig. 33).

Fig. 33:
Energy balance of
different materials
(GMT: glass mat-
filled thermoplastics)
■ *Components*
  manufacture
■ *Driving mode*
■ *Savings over steel*
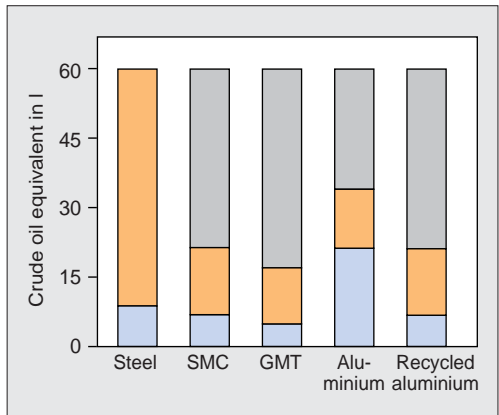
• The excellent impact resistance of GRP offers protection against damage by stone chips and hailstones.
• GRP offers a virtually unlimited freedom of design. Complicated structures and shapes can be produced in one single production step. The aerodynamic and design requirements of modern vehicles can be met without any problem.
• GRP offers good corrosion and weather resistance, which guarantees a very long service life.

- The excellent class A surface quality makes it possible to paint GRP in modern lacquering installations.
- Special resin systems are available for cases where a high fire-resistance is needed, such as in the railway industry.
- GRP is a good conductor for electromagnetic waves. This is rapidly becoming a major advantage in the car industry where antennas and transmitters for radio, mobile phones and satellite navigation are integrated in GRP parts, e.g. the boot lid of passenger cars.

Process equipment

The good corrosion resistance of unsaturated polyester resins and vinyl ester resins make them very suitable for the construction of chemical process equipment.

The first applications were developed in the 1960s for the pulp and paper industry. Very corrosive chemicals were used in bleaching pulp. The usual equipment in those days was constructed of wood or sheet metal and showed severe corrosion problems. The combination of corrosion-resistant materials (bisphenol-A-based resins and later vinyl ester resins) and a very flexible processing technique such as filament winding made it possible for complicated pieces of process equipment to be made that were cheaper, lighter and very corrosion resistant.

Pulp and paper industry

Another early application for corrosion-resistant resins was the ore industry. Many metals are extracted form natural ores by reactions with strong acids or cyanide solutions. Extraction vessels made of bisphenol A resins show a very long service life. In comparison, vessels made of highly corrosion-resistant metal alloys such as stainless steel,

Extraction of metals

Hastelloy®, etc., would be much more expensive and more difficult to handle and install.

Incineration plants
The modern vinyl ester formulations also have a good thermal stability. They are used extensively now in the construction of process equipment which runs at operating temperatures of 160°C and higher. The burning of municipal waste in modern waste incineration plants is a good example of the application of such corrosion-resistant systems. The flue gases of these incinerators have to be cleaned thoroughly before letting them escape into the atmosphere. Acid components in the flue gases are washed out at operating temperatures of 160 to 180°C.

Filament winding technique
Many process equipment parts are cylindrically shaped. Filament winding is therefore the best production technique in this case. The construction is done in several steps. On the cylindrical mould, also called the mandrel, a release film is wound, usually made of polyethylene terephthalate (PET). On this film the first layer of vinyl ester resin is applied in a thickness of approx. 500 to 1000 μm. In the resin layer, a thin non-woven glass fibre veil is wound to give the resin layer a better impact behaviour.

Structure of the vessel wall
After an initial cure of the vinyl ester layer, a corrosion barrier is built up with chopped glass fibre and vinyl ester resin, usually to a total layer thickness of approx. 3 mm. This layer is also left to cure. Finally, a constructive layer is applied to a thickness which is necessary for the specific piece of equipment. The wall thickness can become as high as 50 to 90 mm, depending on the size of the tank, the height and the internal pressure. The constructive layer does not necessarily have to be made from vinyl ester resin. It is not subjected to the same corrosive environment

Fig. 34:
Process plant made
of vinyl ester resin

as the inside of the vessel. Figure 34 shows a purification system used to clean gas with sulphuric acid.

Another important application where corrosion resistance plays an important role is the use of polyester or vinyl ester resins in pipelines for the transport of sewage water or chemicals. An established process for the production of long lengths of pipe is the continuous filament winding or Drostholm process (see also chapter "Filament winding", p. 38).

Sewer relining

An interesting application of growing importance for unsaturated polyester resins is the relining of damaged or worn sewer systems.

The usual way to repair such a sewer system is by digging up the streets and replacing the whole system with new concrete structures. Such complicated and time-consuming

Usual procedure

operations are hardly possible anymore in today's traffic-laden cities.

New principle In the 1970s, a new approach to the repair of sewer systems was developed in the UK. The idea is as simple as it is ingenious: A non-woven felt is sewn into a tube with a watertight coating on the outside. The felt tube is impregnated with polyester resin which already contains a high-temperature curing system. The felt tube is inserted inside out into the sewer system through a manhole (Fig. 35) so that the watertight layer is now at the inside. In one go, lengths of 600 m can be inserted. As soon as the felt is inserted
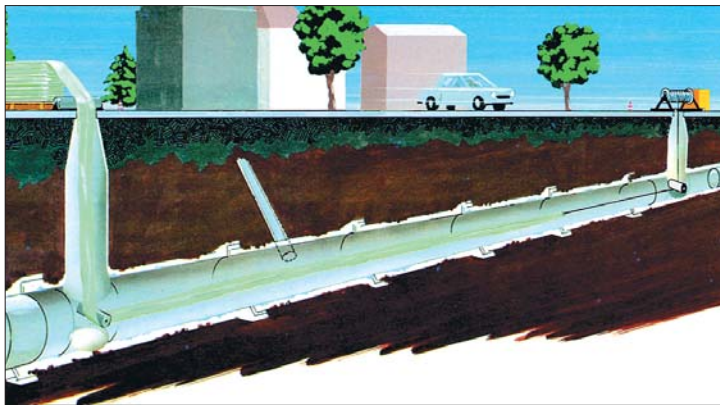
Fig. 35:
The sewer relining principle

completely, the curing is started by circulating hot water through the pipe. Within 24 hours the sewer is completely relined and the street is open to traffic again.

Process variants After this initial invention many variations on the relining technology were developed. The use of hot water to cure the lining is an energy-consuming operation. Alternative systems use resins that are equipped with light initiators. The lining is inflated by means of compressed air to allow remote-controlled

robots equipped with UV lamps to navigate the sewers. The UV light serves to cure the resin. On the reinforcement side, variations have been developed with woven glass fibre tubes.

Wind energy plants

Unsaturated polyester resins are used in a number of applications associated with energy generation. The most striking one is the production of windmill blades (Fig. 36).

Windmill blades are aerodynamically and geometrically complicated shapes. Besides this, the mechanical strength and stiffness, weather resistance and impact behaviour are important parameters for modern windmill blades. Other important aspects are lightweight construction, to achieve the maximum energy yield and freedom of maintenance. Glass fibre-reinforced polyester resins proved to be the best construction material for the production of these modern windmill blades.

Fig. 36:
Wind energy plant

The energy output of a modern windmill has changed dramatically in the last 10 years. In 1990, a capacity of 100 kW was considered state of the art; nowadays, a windmill generates as much as 3 MW of energy. The total span of the blades from tip to tip is between 60 and 80 m. This development continues; offshore installations are on the drawing board with planned capacities of 5 MW per windmill. In this case, the total span of the blades increases to more than 90 m, even examinations on spans of more than 100 m are already made.

Increasing capacity

The forces exercised by the wind on blades of this length put very high demands on the construction material. Fatigue resistance is paramount; even after many years of

Demands on the material

operation, the blades must remain stiff enough to withstand bending forces by full wind.

Storage and transport of materials

Depending on the substance to be stored or transported in a GRP container, specific requirements are necessary. The storage of foodstuffs, for instance, requires that no materials migrate from the container or the environment into the foodstuff. GRP is, often in combination with other materials (e.g. polyurethane foam), very suitable for the production of storage and transport containers. GRP is therefore suitable for the manufacture of, for example:

Fig. 37: Storage tanks for chemicals

- containers and vessels for the transport of dangerous goods by lorry or ship;
- storage bins and silos for electrolysis systems, water treatment plants (including industrial demineralisation plants), and for the textile, paper and pulp industries;
- containers used for processing and storing products such as sugar, fruit juice, bread and pastries, meat, animal fodder, fertilisers, cereals, de-icing salt, sand, limestone powder and aluminium sulphate.

Other main applications are containers and pipes for storing and conveying acids, caustic solutions, liquids and gases of varying temperature as well as pipes for long-distance energy plants and for sewage systems (Fig. 37).

Environmental aspects

Styrene emission

Styrene is a colourless to slightly yellow, rather volatile liquid with a sweet and pungent odour. It has a boiling point of approx. 145°C and a vapour pressure of 10 hPa at 20°C. Styrene has a very low odour threshold, i.e. the presence of styrene can already be noticed at concentrations that are as low as 0.15 ppm (parts per million) or 0.64 mg/m³.

Although styrene is found in nature (e.g. many foods such as strawberries, beans, nuts, beer, wine, coffee beans and cinnamon contain low concentrations of styrene), most people never come directly in contact with this raw material except in its chemically altered form. The situation is different for people who work in factories where it is produced. In all European countries, strict regulations to limit worker exposure to styrene are in force. In most cases, the MAC value (the maximum allowable concentration) for styrene is limited to between 20 and 50 ppm. Although injurious to the health in high concentrations, there is no danger involved in handling styrene provided the specified MAC values are observed.

When processing unsaturated polyester resins in open processes such as hand lay-up or spray-up, a part of the styrene will evaporate. The styrene emission from a polyester resin has to be split in two parts, i.e. dynamic emission and static emission.

As long as a resin is processed, e.g. by spraying or rolling, the surface of the resin is constantly renewed and styrene will continue to evaporate. This is called dynamic emission. As

soon as the resin is left to cure, the evaporation of styrene is called static emission. The amount of styrene that evaporates depends on several factors. A few of them will be explained.

The processing technique

The different types of processes are associated with different styrene emission rates (Table 3). The emission rate with open processes is generally higher than with closed processes, because during the build-up of the laminate, the liquid resin is exposed to air and a part of the styrene can evaporate. Notwithstanding this, the emission rate of different types of open processes also varies widely. This is due to the fact that the styrene evaporates on the surface of the laminate. If the resin is applied

Decisive: Size of the surface …

Processing technique	Standard resin	LSE resin	LSE-DCPD resin
Hand lay-up technique	3.0	1.0	0.8
Spray-up technique	6.0	3.0	2.4
Pressing process	1.0	1.0	1.0
Injection process	0.5	0.5	0.5
Filament winding	4.0	3.0	2.4
Pultrusion	3.0	3.0	3.0
Continuous lamination	1.0	1.0	1.0

Table 3:
Styrene emission rate for different processing techniques dependent on the type of resin

in thin layers or in a fine spray, as when applying a gelcoat with a spray gun, large amounts of styrene can escape. If, on the other hand, the surface area of the resin related to the amount of material processed is small, then the emission rate is also correspondingly low.

The highest emission is found when using the spray-up technique. The resin is atomised in

more or less fine droplets. These droplets have a high surface area per kg of product. Hence the emission per kg of resin processed is high. Modern spray equipment is equipped with nozzles that generate bigger droplets of resin. This brings down the emission rate considerably.

During rolling-out of a laminate, the styrene emission is also relatively high because the surface of the resin is renewed constantly. As soon as the laminate is consolidated and left to cure, the emission of styrene will decrease.

The curing speed

Styrene evaporates from the surface of the laminate as long as the resin is liquid. A certain gel time is of course necessary in order to finish the laminating work. As soon as the work is finished, the gel time should be finished also. As soon as a resin starts to gel, the styrene emission reduces rapidly. It is therefore important to adjust the gel time and the curing speed as exactly as possible by using the proper curing system.

… consistency of the resin …

The ambient temperature

A higher ambient temperature results in a higher vapour pressure of styrene and thus also in a higher evaporation of styrene from the liquid surface. The gel time of the resin will still be more or less the same as at lower temperatures, because it determines the working time. The net effect of a higher ambient temperature is thus a higher emission of styrene.

… and temperature

Measures to reduce styrene emissions

There are several ways to reduce styrene emission during the processing of polyester resins. The first possibility is of course to add less styrene to a polyester resin. A typical resin

Reduction of the styrene content

contains approx. 40% of styrene. This amount is not needed in its entirety for the cross-linking of the resins, but rather also to give the resin its proper viscosity to facilitate processing. When lower styrene amounts are used in a resin formulation, the result will be a higher viscosity.

A reduction of the styrene content of polyester resins can only be achieved by modifying the polymer backbone of the resins. Recent developments have been published in which resins are described with contents of 25 to 30% by weight.

DCPD-based resins generally have a slightly lower polymer viscosity and contain approx. 35% styrene by weight. Both types of resins show a lower dynamic emission of styrene (see also Table 3, p. 60).

Addition of film-forming substances

A widely used way of reducing the styrene emission is the use of film-forming additives in the resin. The principle of these film-forming additives is a partial solubility of the additive in styrene. It is added to a resin in low quantities (max. 1%). The resins obtained in such a way are called low-styrene-emission resins or LSE resins.
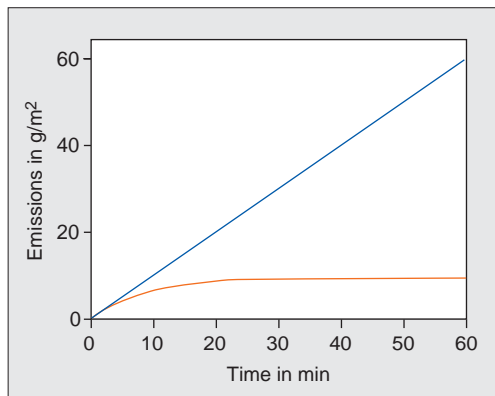

Fig. 38:
Effect of LSE additives on styrene emission

A frequently used film-forming additive is paraffin with a melting point of approx. 56°C. This type of paraffin is only slightly soluble in styrene. The paraffin additive is only active in the static phase of the emission. Once the resin is rolled and de-aerated, it is left to cure. Some styrene will still evaporate from the surface. The effect is that the paraffin additive separates from the solution and forms a film on the surface. This film stops a further evaporation of the styrene (Fig. 38).

Use of light-curable resins

A very effective way to reduce the styrene emission is the use of light-curable resins. Polyester resins are usually cured by means of organic peroxides. An alternative way to cure polyester resins is by using initiators that are activated by visible or ultraviolet light. These initiators are added to the resin during the production phase. As long as the resin is stored in the dark, it will remain liquid. When working with light-curable resins in dimmed light conditions, the gel time is very long. The resins cure quickly as soon as they are subjected to a bright visible or ultraviolet light. The surface of the resin cures very quickly, forming a film of cured resin on top. This will stop the styrene emission almost instantly.

Limitations

Light-curable resins have only found a limited use in practice. Complicated products cannot be made easily with light-curable resins, as an equal light intensity on all parts of a product is difficult to achieve. Furthermore, the use of light-curable resins is restricted to transparent products only. Fillers and pigments cannot be used in the product.

Application of closed-mould techniques

The latest technical developments are in the direction of using closed-mould techniques for the production of composite parts. This will bring down the emission of styrene.

Occupational health aspects

Investigations over many years under large numbers of polyester workers have not shown any evidence that styrene has carcinogenic or mutagenic effects. In spite of this, most countries have strict rules regarding the workplace exposure to styrene.

Ways of styrene absorption

The absorption of styrene in the human body can happen in two ways, i.e. through the inhalation of styrene vapour or through dermal exposure. Styrene metabolises rapidly in the human body. It is broken down into mandelic acid and phenyl glyoxilic acid, two substances that are excreted along with urine.

Effects on the human organism

The inhalation of styrene can cause narcotic effects that are similar to the effects of alcohol. Depending on the concentration of styrene in the air, the effects can vary from a light dizziness to headache and loss of concentration. The intake of styrene through the skin is considerably lower than through inhalation. Wearing styrene-impermeable gloves will give sufficient protection.

Protective measures

Working with open-mould methods is the main cause for the exposure to styrene. The use of low-styrene-emission (LSE) resins has considerably reduced the exposure to styrene in the last 10 to 20 years. A major improvement here is the switch to closed-mould methods such as vacuum injection and RTM. These technologies are rapidly growing. They lead not only to a lower occupational exposure, but also to better and more consistent quality of the products made of unsaturated polyester resin.

Outlook

Although unsaturated polyester resins are considered to be mature products, there are still new markets and applications opening up where these products will be used. Properties such as light weight, corrosion resistance and versatility in processing methods are the strong points when considering UP resins as a construction material. A few interesting new applications will be described below in more detail.

Offshore wind energy plants

The market for windmill blades is still booming. The energy produced by wind energy plants reached a figure of 20,000 MW worldwide in the year 2000. All over the world, this clean and renewable source of energy is being applied in rapidly increasing numbers. The projected growth figures are ambitious; the European Wind Energy Association EWEA estimates that by the year 2010, there will be an installed capacity of 60,000 MW in Europe alone.

Increasing demand for wind energy

The increasing demand for wind energy will lead to bigger installations built in areas where the highest wind potential is available. Building offshore will become a major new challenge for the technology of wind energy. However, the conditions under which offshore windmill plants are run are very rough and the maximum diameter for a windmill is still increasing. Blade lengths of 45 m are now on the drawing board.

Operation under extreme conditions

In order to meet the requirements on mechanical strength and stiffness, materials and processes must be selected that permit the manufacture of lighter and more stable wind-

mill blades which are capable of operating over prolonged periods without the need for maintenance. This is why the production process for windmill blades is changing from the traditional open-mould techniques such as hand lay-up and spray-up to closed-mould techniques such as vacuum injection. Traditional production methods such as hand lay-up are no longer good enough to ensure a consistent quality and vacuum injection will be the key process for the coming years.

Concrete reinforcements

Concrete is by far the most important construction material for buildings and other civil structures. The strength of concrete is to a

Fig. 39:
Vinyl ester rebars
in a bridge deck
construction

large extent determined by the use of steel bars as reinforcement. Steel is sensitive to corrosion, but the alkaline environment in concrete prevents the steel reinforcement from rusting away. In some cases, however, concrete is used in very aggressive environments. Bridge decks are made of concrete. In the wintertime, salt is sprayed on the deck to prevent slippery surfaces. This salt solution can penetrate into the concrete and act very aggressive on the steel reinforcement.

Replacement of corrosion-sensitive steel bars …

In recent years, reinforcing bars have been developed that are based on glass fibre and vinyl ester resin. These "rebars" are now used for the construction of bridge decks and other corrosion-sensitive applications of concrete (Fig. 39).

… by "rebars"

Butane storage tanks

Butane and propane sold to the private market is normally packed in steel bottles of 10 to 25 litres. The steel bottles are heavy (the weight of the packing is more than that of the content) and behave very dangerously in a fire. When heated in a fire, steel butane or propane bottles explode. In Sweden, a company has developed a butane bottle of glass fibre-reinforced UP resin. The bottle weighs one third of a steel bottle and is safe in a fire. When exposed to a fire it does not explode, but rather cracks slowly, allowing the burning butane to seep away in a very controlled manner.

Fig. 40:
Glass fibre-reinforced UP-resin butane tank

An additional advantage is the transparency of the bottle. The liquid level inside the bottle can be checked easily from the outside (Fig. 40).

Automotive industry

In the automotive industry, fuel efficiency, lightweight materials and design freedom are

Use of the low weight …

key success factors where composites can play an important role. Due to the high production volume of automotive parts, hot press moulding is the preferred production technique for these parts. There are, however, alternatives for SMC and BMC on the drawing board.

… and the high stiffness of GRP parts

Resin transfer moulding is an alternative technique that can be used for making high-strength constructions which make cars lighter and stiffer. The technique is still not suitable for large-volume applications, but the developments are moving rapidly in the right direction.

Bridge construction

New application fields …

Steel and concrete have been the material of choice for the construction of bridges for many decades. These materials, however, have their particular problems such as their weight and corrosion-susceptibility.

Composite bridges show considerable potential to replace steel and concrete bridges. De-

Fig. 41:
Pedestrian bridge made from a composite material

signing a composite bridge is a rather new engineering skill, but rapid progress is being made. All over the world, many composite bridges have already been installed for pedestrians and light traffic (Fig. 41). Heavier constructions are on the drawing board already and will soon be realised. In many cases, pultruded profiles serve as the base construction material for the structural stiffness of the bridge.

… with considerable potential

Use of alternative materials

In this booklet, we have talked almost exclusively about UP resins and glass fibres. Both materials, however, are based on natural resources that are not renewable, or their production contributes to the generation of greenhouse gases such as CO_2.

Modern chemistry is now looking into renewable resources for their raw materials. Natural fibres such as flax and hemp are already being used in certain applications where biodegradability plays an important role. Resin systems are being developed that are based on agricultural raw materials such as soybean oil.

The companies behind this book

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In 1883, two young and enterprising men – Ludwig Büsing and Friedrich Fasch – formed a wholesale establishment for dyes, chemicals and oil. The work they started then is now being continued by 450 staff.

Proud and aware of the responsibilities associated with the almost 120-years-old BÜFA tradition, the five business divisions operate independently and with an open-mindedness for new developments around the world. The founding fathers already traded in chemicals and manufactured cleaning products. Glass materials were added to the range in the 1930s, and reactive resins in the early 1960s. The formulation of in-house polyurethane systems began in 1969.

BÜFA Reaktionsharze GmbH & Co. KG has meanwhile developed into one of the leading manufacturers of speciality products based on unsaturated polyester and vinyl ester resins. In cooperation with DSM Composite Resins AG, BÜFA produces gelcoats, bonding pastes, repair putties, pigment pastes and special resins on a large scale in its new plant in Rastede close to Oldenburg.

The range of reinforcing materials, peroxides, acrylic pastes, releasing agents and further products made by other renowned business partners and available from BÜFA makes BÜFA the classic one-stop shopping partner with a leading position in Europe.

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DSM Composite Resins is the leading European producer of solutions for the composite resin industry. With more than 500 employees, DSM Composite Resins wants to continuously improve its products and services.

DSM Composite Resins has a single central office in Switzerland, at the heart of Europe. From here the company coordinates all its commercial and logistical functions and supports the various production sites in the Netherlands, Britain, Italy, Spain and France, as well as its local Customer Competence Centres in Zwolle (Netherlands), Deeside (UK) and Como (Italy).

DSM Composite Resins offers a wide range of chemistries and formulations, enabling a broad range of process variables and end-use properties. Chemistries include unsaturated polyesters, vinyl esters, hybrids and specialty resins for structural resins and gelcoat products. In addition, we use polyurethanes, polyamides, polyvinylacetate and saturated polyesters in sizings, binders and plasticizers.

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