

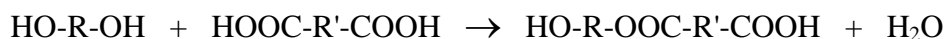
POLYESTERS FOR USE IN THE FIBREGLASS INDUSTRY

The word fibreglass refers to any substance composed of glass fibres, usually held in a polymer resin matrix (base). However, fibreglass has also come to mean any similar fibre-based material, with fibres of various different substances. This material can be made to a variety of flexibilities, and is characterised by its strength and resistance to heat. It can also be made so that it is resistant to certain chemicals and to U.V. light, with these variations due to the original monomer mixture chosen.

This article looks at the production of polyester resins, which are made from difunctional alcohols and acids in a two step process:

Step 1 - Polymerisation

The polyester is formed by the condensation reaction:

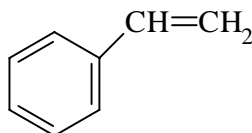


The ester thus formed contains an alcohol group and an acid group, which can then react further, forming a polymer:



Step 2 - Curing

To make the polymer stronger and more resistant to heat, it is then 'cured' by reacting it with a monomer such as styrene in the presence of a peroxide catalyst.



styrene

This results in the polyester chains crosslinking to form a harder, more durable, thermo-setting polymer.

The waste gases are then scrubbed to remove pollutants, and the liquids are left to settle (removing solid matter) and are neutralised before they are disposed of into the environment.

INTRODUCTION

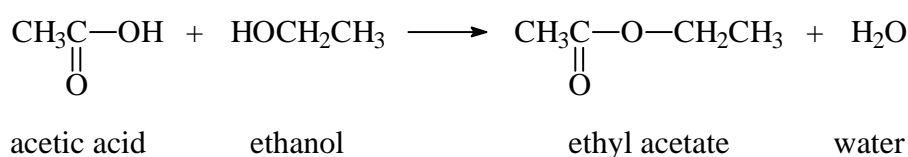
Fibreglass refers to any substance composed of fibres in a thermo-setting polymer matrix. The fibres are usually glass, but they can also be carbon, "Kevlar" (an aromatic polyamide) or any other suitable fibre. The polymer can be any thermo-setting resin¹ but the two main types used are polyester and epoxy resins. By careful selection of raw materials these differences can be exploited to allow items as diverse as kitchen sinks and racing boats to be economically and reliably manufactured.

¹A thermo-setting resin is any polymer that doesn't melt when heated.

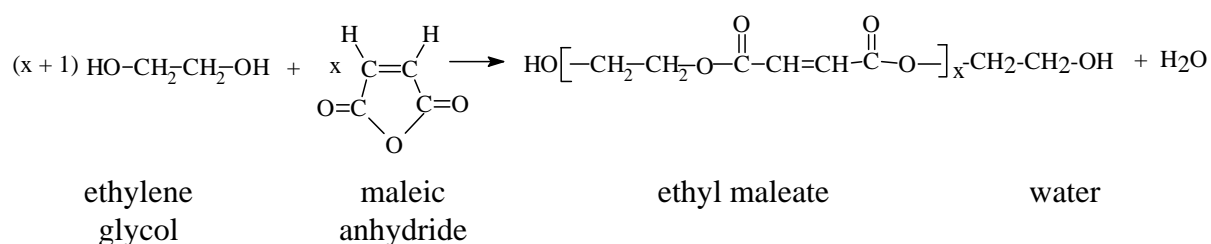
Polyesters, the polymer resins that are the focus of this article, have been made commercially in the U.K. and the U.S.A. since 1945, and have been made in New Zealand since the 1960s.

Research is continually undertaken to establish new polyesters and new processing techniques to suit changing market requirements.

The term *polymer* refers to any large chain-like molecule consisting of many single repeating units (from the Greek *poly*, meaning many). In the case of polyesters, the repeating unit is an ester linkage formed in the same way as simple esters but using a compound with several functional groups, rather than the mono-functional chemicals normally found in the manufacture of "pure chemicals". For example, the *pure* ester ethyl acetate is synthesised as follows:



But to synthesise a *polyester*, difunctional acids and alcohols are needed:



Raw materials

The raw materials required for the manufacture of polyester resins are almost entirely derived from coal and petroleum bases, as can be seen in **Figure 1**.

THE MANUFACTURING PROCESS

Polyester resins are polyesters that have been 'cured', i.e. treated with a monomer that causes the chains to crosslink. This results in a material that is hard and durable, and that will not melt on heating - a thermo-setting plastic.

Step 1 - Polymerisation

Polyesters are formed by reacting a difunctional alcohol with a difunctional acid at temperatures between 170°C and 240°C. The exact temperature depends on the ingredients chosen and the final properties required. The reaction is carried out in a reaction vessel such as the one shown schematically in **Figure 2**. Often reaction catalysts are required to speed up the reaction, and in all cases a flow of inert gas (usually nitrogen) is used to help with the removal of water from the kettle and to exclude oxygen from the process. Air in the kettle during the reaction causes unwanted side reactions which can cause anything from a simple discolouration of the polymer to gelation of the entire batch.

As can be seen from equation (1), water is a by-product of the reaction and must be removed from the kettle by distillation to allow the process to proceed.

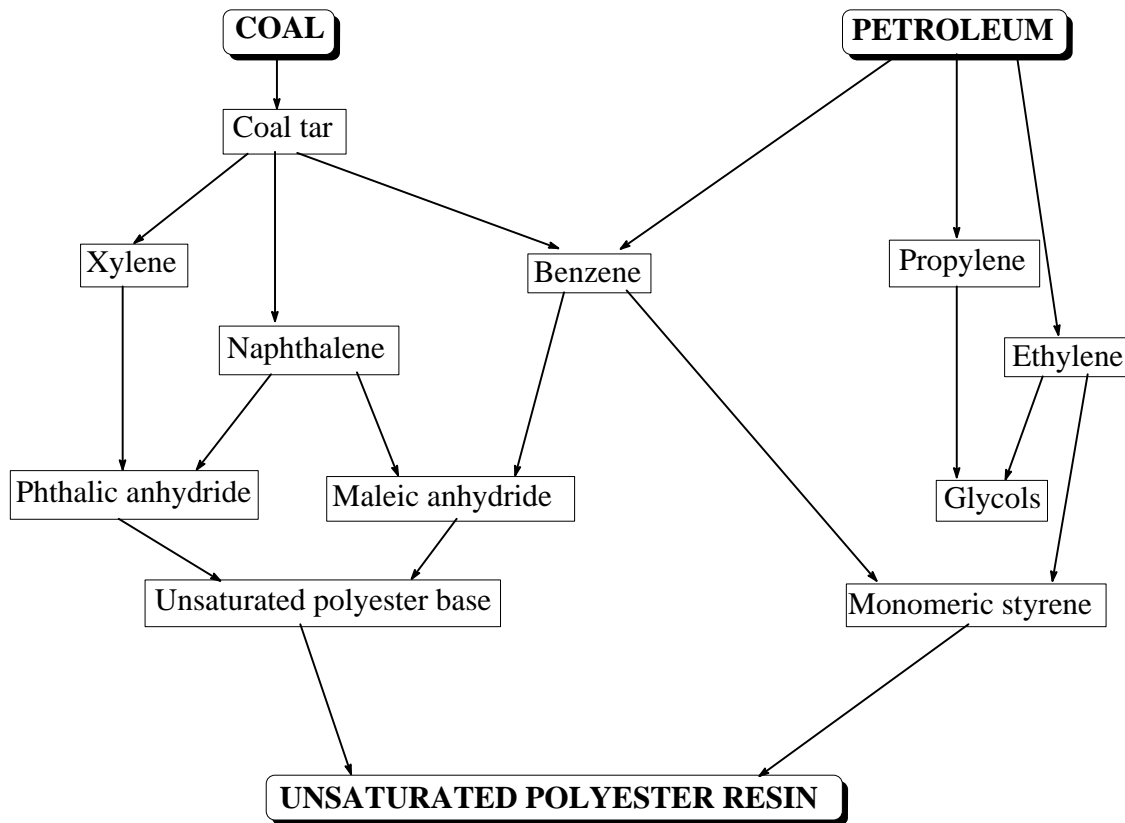


Figure 1 - The production of the raw materials from coal and petroleum

Choosing the monomers

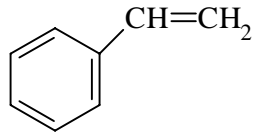
Polyesters can be either saturated (no double bonds in the polyester backbone), or unsaturated (with double bonds). In order to crosslink with unsaturated monomers, such as styrene, the polyester must have double bonds within its backbone with which the monomer can react. These are usually formed from the maleic anhydride monomer, and enable the polyester to be used in the manufacture of fibre reinforced items.

The range of chemicals that the polymer chemist can call on to fabricate a polyester with specific properties is quite considerable. The common monomers are listed in **Tables 1 and 2**.

By varying the ratios of these ingredients the polyester chemist can "engineer" a resin that can be anything from soft and rubber-like through to hard and glass-like. Fire retardant properties can also be built in, as can resistance to U.V. light, to water and to certain chemicals.

Step 2 - Curing

Once the required end point has been reached the batch is cooled (although not to room temperature as this would solidify most polyesters) and dissolved in a reactive diluent. Monomeric styrene is the usual monomer for this process, although acrylates and methacrylates are used in specialty resins. This then gives a solution of the polyester which is



styrene

liquid at room temperature and which, after the addition of accelerators and catalysts, will cure to a thermoset polymer. This liquid is used to impregnate fibres so that when the polymer is cured a fibreglass item will be formed.

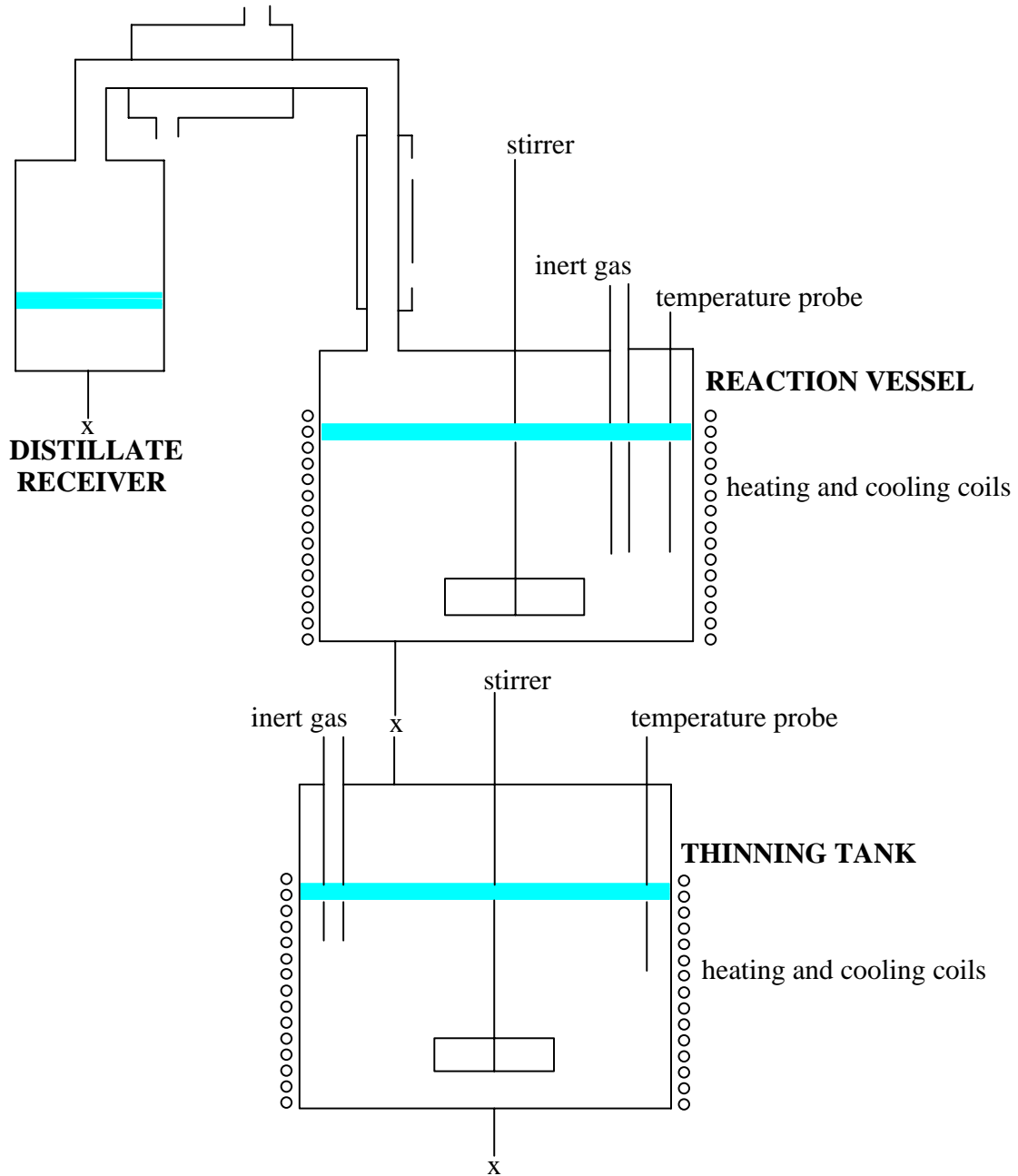


Figure 2 - Schematic representation of the polyester production process

Table 1 - Common acid monomers used in polyester manufacture

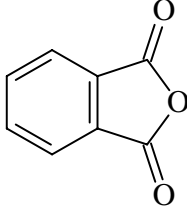
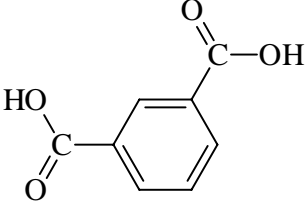
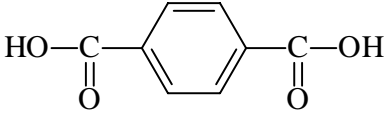
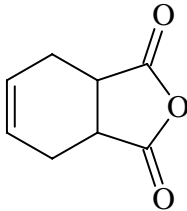
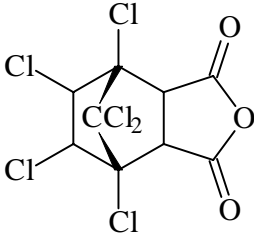
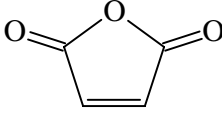
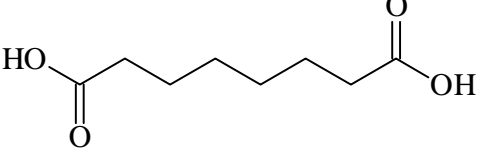
Name	Structure
phthalic anhydride	
isophthalic acid	
terephthalic acid	
tetrahydrophthalic anhydride	
hexachloroendomethylenetetrahydrophthalic anhydride	
maleic anhydride	
adipic acid	

Table 2 - Common glycols used in polyester manufacture

Name	Structure
ethylene glycol	
diethylene glycol	
propylene glycol	
dipropylene glycol	
neopentyl glycol	
hexan-1,6-diol	

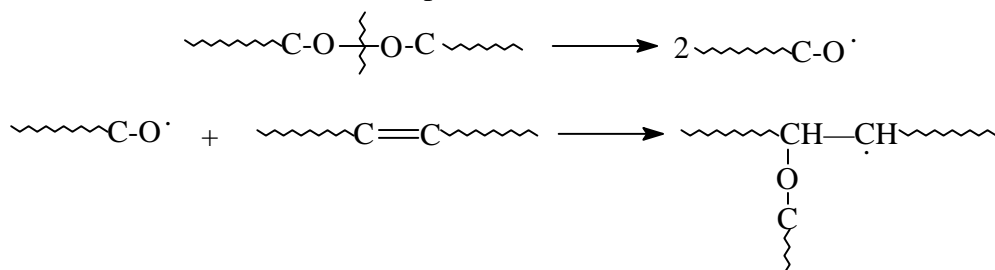
Polyesters cure by a three step free radical process, whereas polymers such as epoxides or polyurethanes cure by an addition process.

Free radical polymerisation

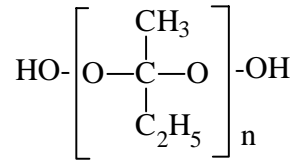
Peroxides which have the general structure R-O-O-R cleave between the oxygen atoms to give the oxy-radical R-O•, and these free radicals attack the double bond on both the polyester backbone and the styrene monomer.

1) Initiation

Firstly the free radicals are formed from peroxides:



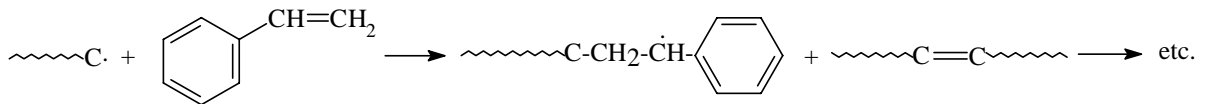
A typical peroxide for the room temperature curing of polyesters is methyl ethyl ketone peroxide (MEKP):



where $n = 1 - 4$

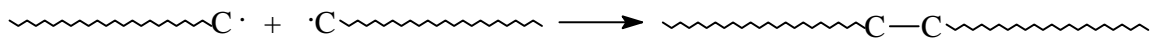
2) Propagation

The chain then grows by propagation. In this process the polymeric free radical continues to react with further double bonds in the polyester/styrene mix:



3) Termination

In the final step in this process free radicals react with other free radicals or chain termination species in the polymer mix.



This gives the cured polyester, which has a three dimensional 'net' type of structure, the physical properties of which are dependent on the type and ratios of the various acids and glycols used in the initial formulation.

Thus the curing process can be represented by **Figure 3**.

THE ROLE OF THE LABORATORY

The reaction is monitored during processing by taking samples from the kettle and testing them for Acid Value (AV) and viscosity. As the reaction proceeds the acid is used up, and hence the acidity in the kettle reduces. In addition, the viscosity of the resin increases with the molecular weight of the polymer being formed. Other parameters could also be monitored, such as OH value, but the acid value is a quick and easy test that can be carried out in the plant during manufacture.

After a number of polyesters of the same type have been made, a chart of AV vs. viscosity can be plotted to ensure subsequent batches are reacting in the required manner.

ENVIRONMENTAL IMPLICATIONS

As there are by-products from the reaction (even under the most controlled conditions) the distillate and all the gases require careful treatment before disposal. The gases are released into the atmosphere after scrubbing, which removes from the gas stream all the organic vapours that have been produced. The distillates are neutralised, and particulate matter is allowed to settle out before the liquid is disposed of into trades waste drains.

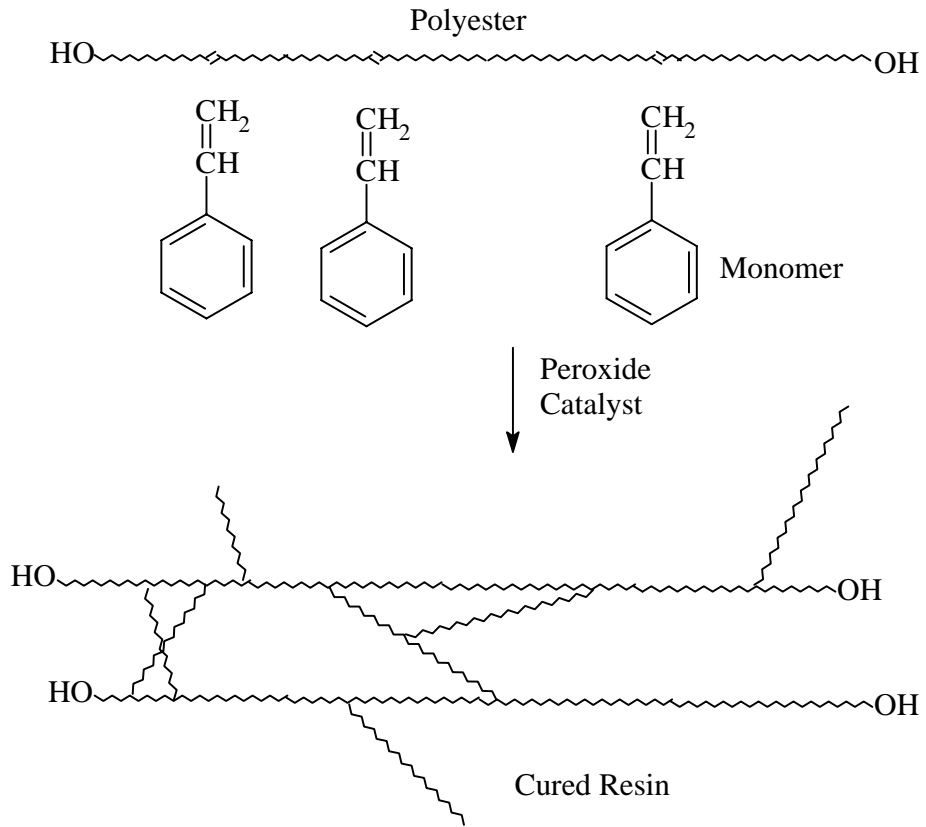


Figure 3 - The curing process

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