A103

Polyester resin

Document Type	Article
Document Identifier	103
Relevant Class	Material
Tags	• Object • Material • Matrix • Thermoset polymers

Properties
Appearance
Usually clear, but can be dyed different colours
State
Viscous liquid at room temperature
Density
1100 - 1200 kg/m^3
Flash point
25 - 40 °C
Hazards
Globally harmonized system (GHS)

- ◆
- ◆
- ◆
- Eye irritant cat. 2
- Skin irritant cat. 2
- Respiratory sensitizer
- Flammable liquid cat. 3

Introduction[edit | edit source]

Polyester resins are used extensively in industrial applications due to their ease of fabrication, good all-around properties, and lower cost than epoxy and vinylester resins. They were the second thermoset resins discovered in the early 1940s after phenolic resins and are today the most used thermoset resins.

Scope[edit | edit source]

This page presents the formulation, processing and design properties, advantages and limitations when compared with other thermoset resin systems (e.g. epoxy, phenolic resins, etc.), typical applications, and key considerations for polyester resins. Specifics about the microstructures, thermal transitions and cure kinetics of thermoset resins are given in the Foundational Knowledge volume.

Significance[edit | edit source]

Polyester resins are commonly used to produce glass fiber reinforced polymer (GFRP) parts (see for example the following case study: Troubleshooting of room temperature processes for large recreational and industrial parts).

Prerequisites[edit | edit source]

Recommended documents to review before, or in parallel with this document:

- Thermoset polymers
- Degree of cure
- Heat of reaction
- Thermal phase transitions of polymers

Object Description[edit | edit source]

Level I
Level II
Level III

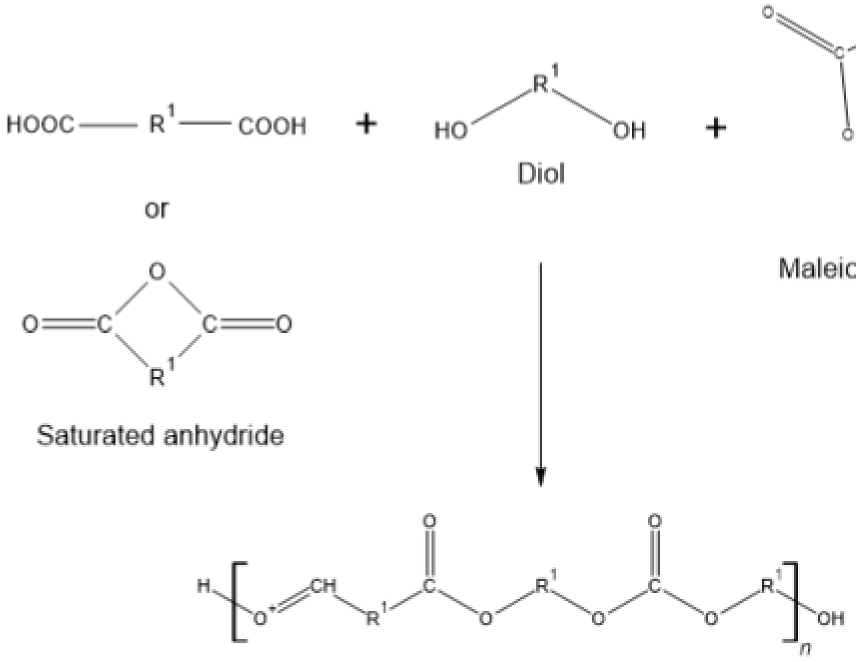
Unsaturated polyester (UPE) resins have two primary constituents, i.e a polyester and a reactive crosslinking diluent. Most commercial UPR resins contain 60 to 70 wt.% of polyester dissolved in styrene, but it is possible to use other vinyl monomers, such as methyl styrene and alkyl methacrylate monomers. The crosslinking diluent serves two functions. It dissolves the polyester polymer and reduce its viscosity which allows its liquid processing under ambient conditions. It also reacts with the unsaturated carbon-carbon double bonds of the polyester polymer, which leads to the solidification of the resin during processing. For room-temperature cure UPE resins, the crosslinking reaction is initiated by adding an initiator, usually a peroxide. The initiator decomposes into free radicals which react with the double bonds of the polymer and then form new chemical bonds with the crosslinking agent. In addition, an inhibitor and an accelerator can be added to respectively prevent premature gelling, i.e. to extend shelf-life, and to accelerate the decomposition of the initiator, and so to speed up the crosslinking reaction. The most commonly used inhibitor and accelerator are hydroquinone and cobalt napthenate.

Unsaturated polyester resins are extremely versatile. An infinite number of UPE formulations can be created by modifying the type and concentration of the UPE polymer, reactive diluent, initiator, inhibitor and accelerator. The UPE industry has not created any standard type of product or formal classification which means there is hardly any identical UPE resins from two different producers.

In most cases, polyester resins contain 60 to 70 wt.% of an unsaturated polyester (UPE) polymer dissolved in a reactive crosslinking diluent, such as styrene. The crosslinking agent serves two functions. It dissolves the polyester polymer, which allows the liquid processing of a typically highly viscous polymer under ambient conditions. It also reacts with the unsaturated carbon-carbon double bonds of the polyester polymer, which leads to the solidification of the resin during processing. The crosslinking reaction is initiated by adding an initiator, usually a peroxide. The initiator decomposes into free radicals which react with the double bonds of the polymer and then form new chemical bonds with the crosslinking agent. Note that the crosslinking agent can also undergo homopolymerization depending on the reaction conditions. In addition, an inhibitor and an accelerator can be added to respectively prevent premature gelling, i.e. to extend shelf-life, and to accelerate the decomposition of the initiator, and so to speed up the crosslinking reaction. The most commonly used inhibitor and accelerator are hydroquinone and cobalt napthenate.

Unsaturated Polyester[edit | edit source]

Unsaturated polyester (UPE) polymers are prepared through an esterification reaction of a diacid or dianhydride with a dihydroxy compounds (diols) and a maleic anhydride or fumeric acid alcohol, which provides the unsaturated carbon-carbon double bonds. As a result of side reactions, the expected linear structure, is altered with short branches. Unsaturated polyester polymers normally have a low number-average molecular weight of about 700 to 3,000 g/mol with a consistency ranging from a thin liquid, with a viscosity lower than a few Pa.s, to a quite viscous fluid with a viscosity higher than 60 Pa.s [1]. In comparison, epoxy resins are oxirane-containing oligomers (e.g., ethylene oxide, C_2H_4O), which cure through the reaction of epoxide groups with a suitable curing agents, such as amines, thiol and alcohols. The reaction proceeds through the cleavage of the oxirane ring through a nucleophillic addition reaction.



Polymerization reaction of unsaturated polyester resins (adapted from Ratna, 2009)

Depending on the diacid or dihydroxy compounds used for the esterification reaction, thousands of different variations of UPE can be produced and therefore an infinite number of UPE resins. This is indeed the case in the UPE industry where there is hardly any identical product from two different producers (Scheirs & Long, 2003). Nonetheless, three basic types of resins are usually set apart:

- The phthalic anhydride, maleic anhydride and glycol resins, or simply orthophthalic polyester resins. These resins were the first developed unsaturated polyester resins and are thus the standard economic resins referred as “general-purpose resins”. These resins are prone to

hydrolysis by water, and consequently do not have a good resistance to wet environment.
- The isophthalic acid, maleic anhydride and glycol resins, or simply isophthalic polyester resins. Their better resistance to hydrolysis makes them ideal for corrosion-resistant applications.
- The dicyclopentadiene (DCPD)-capped resins, or simply DCPD polyester resins. These unsaturated polyester resins have a highly aliphatic DCPD moiety on both ends. The bulkiness of the DCPD moiety reduces the shrinkage during curing by preventing the polymer chains to stack-up too closely, but make them very brittle due to their ultra-low molecular weights. DCPD polyester resins are primarily used in applications which require an excellent cosmetic appearance.

Crosslinking Agent[edit | edit source]

The reactive monomer also contains an unsaturated group. It has typically a low number-average molecular weight of about 100 g/mol and serves two vital roles for the resin system. It reduces the resin viscosity below 1 Pa.s., facilitating the resin processing and fibre bed impregnation, and acts as a crosslinking agent by forming covalent bonds with the carbon-carbon double bonds of the UPE. The crosslinking reaction ultimately leads to the formation of a solid three dimensional network which is infusible. For most commercial resin, styrene is used, but it is possible to use other monomers, such as vinyl toluene, alpha-methyl styrene, and methyl methacrylate.

The ratio of polyester to reactive monomer ranges from about 75:25 to 50:50 parts by weight leading to an oil-like viscosity around 0.2 to 0.5 Pa.s. Resin colours can range from a very pale yellow to dark amber which can further be affected by the presence of additives such as a cobalt napthenate accelerator (see below).

Inhibitor[edit | edit source]

Inhibitors prevent the UPE polymer and crosslinking agent from reacting prematurely by scavenging free radicals. Free radicals react preferentially with the inhibitor and initiate the crosslinking reaction only after the inhibitor is consumed. The addition of a small amount, less than 500 ppm, can extend the resin shelf-life by more than one year. The most commonly used inhibitors are p-benzoquinone, hydroquinone, and phenothiazine.

Initiator[edit | edit source]

Initiators, sometimes erroneously referred to as catalysts, are used to generate free radicals and so to initiate the crosslinking reaction. The free radicals first consume the inhibitor present in the resin and then react with the UPE polymer. Organic peroxydes are the most commonly used catalysts. Methyl ethyl ketone peroxide (MEKP) when combined with an appropriate promoter decomposes at room temperature, whereas benzoyl peroxide (BPO) and t-butyl peroxide (TBO) decompose at 70°C and 140°C, respectively. Promoters are not generally needed to activate these two peroxides. Some organic peroxides are unstable at room temperature and must be stored under refrigeration. Recommended peroxide concentration range is between 1.25 to 2.5 wt. %. Longer gel times and lower exotherms can be achieved by using cumene hydroperoxyde (CuHP) catalysts. Other types of catalyst or combination of catalyst can be used for specific applications.

Accelerator[edit | edit source]

Accelerators or promoters are usually added by the resin producers to ensure a reasonable curing rate at room temperature. In general, cobalt napthenate, calcium and potassium salts, and amines such as dimethyl aniline or diethyl aniline are used in small amount ranging from 0.02 wt% to 0.3 wt%. Cobalt salts impart a pink to red color to the resin depending on the amount used, while amines usually color polyester resins yellow to brown. The latter can cause accelerated yellowing of cured parts.

Other Additives[edit | edit source]

Other additives include thixotropes and flow modifiers such as fumed silica and magnesium oxide, flames retarders, and ultraviolet stabilizers.

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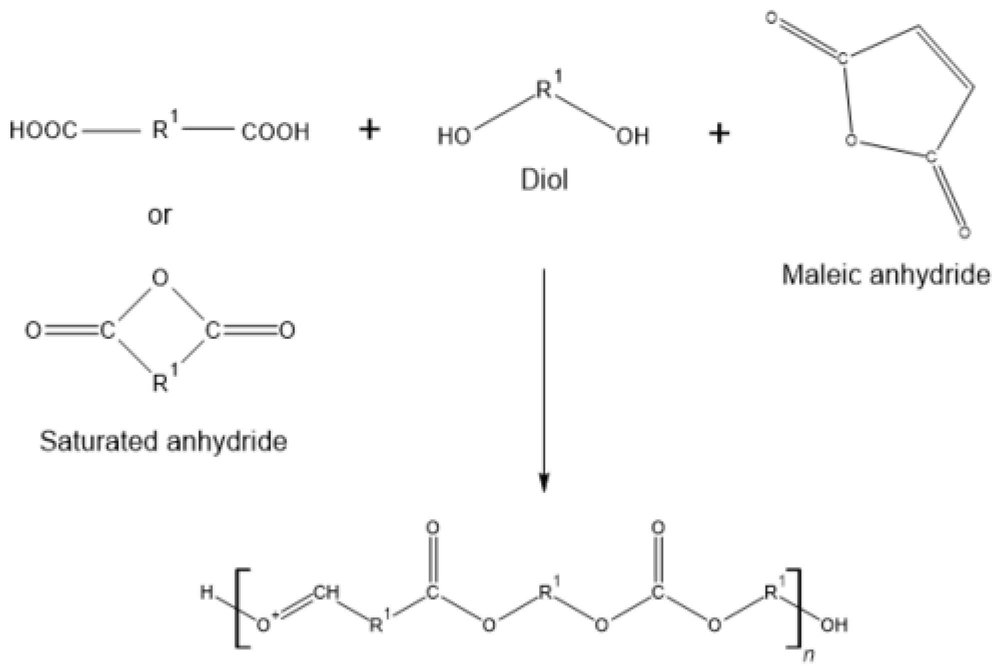

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Cure[edit | edit source]

Structure[edit | edit source]

UPE resin systems contain an unsaturated polyester, a reactive monomer and an inhibitor. When the initiator is added, its decomposition generates free radicals. At the very beginning, which is called the “induction stage”, most of the free radicals formed are consumed by the inhibitor and very little polymerization occurs. Once the inhibitor molecules are depleted, free radicals, produced by the initiator, initiate the cross-linking free radical copolymerization reaction between the unsaturated polyester and the reactive monomer leading to the formation of long-chain molecules. In some cases, these high molecular weight molecules have been observed to separate from the reactive phase to form spherical-type microstructures called “microgel-like” particles. As the polymerization reaction proceeds, the concentration of the microgel-like particles increases, promoting their interparticle cross-linking and clustering which ultimately leads to the formation of a continuous network structure, and thus to the macro-gelation of the curing system. The microgel-like particle formation explains the early gelation compared with the gelation predicted by the Flory-Stockmayer theory for which the formation of a tree-like molecular structure is assumed. The crosslinking-induced phase separation also explains why some UPE resins become opaque at gelation.

Depending on the initial concentration of reactive monomer and formulation, the final network morphology spans from a “tree-like” or “coral-like” microstructure with dumbbell shape and interparticle connections to a flake-type microstructure at high monomer concentration. The addition of an activator also influences the final network morphology. These variations not only affect gelation but also the other physico-chemical properties.

Kinetics[edit | edit source]

Coming soon.

Properties[edit | edit source]

Typical values are given in the table below.

Liquid resin	
Viscosity at room temperature	1.7 4 -10 Pa.s
Cure shrinkage	6 – 7 vol%
Solid resin	
Flexural strength	80 – 125 MPa
Flexural modulus	3.6 – 4 GPa
Tensile strength	45 – 90 MPa
Tensile modulus	3.5 – 3.7 GPa
Elongation at break	1.5 – 2.2 %
Glass transition temperature	50 – 185 °C

Applicable Processing Methods[edit | edit source]

Unsaturated polyester resins can be processed with the following manufacturing methods:

- Hand lay-up
- LCM
- Press forming
- Filament winding
- Pultrusion

Applications[edit | edit source]

Typical sectors or products that use this material include:

- Construction and infrastructure: bathtubs, shower stalls, hot tubs, swimming pools, sinks, countertops, tanks, pipes, bridges
- Ground transportation: body panels, truck body, structural elements
- Marine: hull and decks of powerboats and sailboats, canoes, kayaks
- Sporting goods: surfboards, fishing poles, bowling balls

- Traditional and alternative energy: wind turbine blades

Key Considerations During Use[edit | edit source]

Preparation[edit | edit source]

While utilizing this material, the following are some of the key aspects to focus on to ensure that the quality of the final part is as high as possible. Polyester resins should be stirred mechanically before use. It is also recommended to degas the resin when processed with vacuum-based processes, such as light resin transfer molding. Polyester resins commonly contain 0.05 to 0.1 wt% of moisture upon delivery which can outgas during processing and form porosities.

Storage & Handling[edit | edit source]

Polyester resins should be stored in tightly closed containers, in a dry and well-ventilated preferably below 25 °C. They should be kept away from heat, sparks, flame and other sources of ignition. Styrene-based polyester resins must be stored in light-proof containers. The shelf-life of polyester resins without initiator when stored in a dark and cool environment is typically a few months. The shelf-life is reduced at higher temperatures.

Suppliers[edit | edit source]

Product suppliers[edit | edit source]

- AOC
- Crystic Resin
- Hexcel
- INEOS
- Interplastic Corporation
- Polynt Composites
- Reichhold

Distributors[edit | edit source]

- CompositesOne
- Composites Canada

Expert support providers[edit | edit source]

- Composites Research Network
- Composites Knowledge Network
- Polyvations

References

1. ↑ [1.0] [1.1] [Ref] Ratna, Debdatta (2009). *Handbook of Thermoset Resins*. iSmithers.

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About

Help

For polymer matrix composites (PMCs), resin refers to the matrix; the continuous material phase that binds the reinforcement together, maintains shape, and transfers load. Resins are divided into two main groups: thermosets and thermoplastics.

Thermosets are a class of polymer that undergo polymerization and crosslinking during curing with the aid of a hardening agent and heating or promoter. Initially they behave like a viscous fluid. During curing, they change from viscous fluid to rubbery gel (viscoelastic material) and finally glassy solid.

If heated after curing, initially they become soft and rubbery at high temperatures. If further heated, they do not melt but decompose (burn)

Comes in two parts: part A (resin) and B (hardener). When mixed, curing reaction starts and is not reversible.

Examples include epoxy or polyester.

In composites processing, viscosity is an indicator of how easily the resin matrix will mix with the reinforcement and how well it will stay in place during processing. The lower the viscosity, the more easily resin flows. Resin viscosity ranges considerably across chemistries and formulations.

By scientific definition, viscosity is a measure of a material’s resistance to deformation. For liquids, it is in response to imposed shear stresses.

Liquid Composite Moulding (LCM), a family of infusion processes refers to processes that saturate a dry reinforcement that is on/in the mould by means of a pressure differential (injection pressure, vacuum, combination of both).