UNSATURATED POLYESTER RESIN

Table 3. Optimal Temperature Range of Conventional Catalyst Systems for Unsaturated Polyesters

Catalyst	CAS registry Number	Activator	Processing Temperature, °C
Benzoyl peroxide	[94-36-0]	Dimethylaniline	0–25
Methyl ethyl ketone peroxides (MEKP)	[1338-23-4]	Cobalt octoate	20–25
Cumene hydroperoxide	[80-15-9]	Manganese Naphthenate	25–50
Lauroyl peroxide	[105-74-8]	Heat	50–80
tert-Butyl peroctoate	[13467-82-8]	Heat	80–120
Benzoyl peroxide	[94-36-0]	Heat	80–140
2,5-Dimethyl-2,5-di-2-ethylhexanoylperoxyhexane	[13052-09-0]	Heat	93–150
tert-Butyl perbenzoate	[614-45-9]	Heat	105–150

FORMULATION

ortho-Phthalic Resins

Resins based on *ortho*-phthalic anhydride (Table 1) comprise the largest group of polyester resins and are used in a variety of commercially significant applications, including marine craft, translucent glazing, simulated-marble vanity sets, and buttons. Most laminating and casting processes also rely on both colored and clear gel coats to provide some level of surface protection. The glycol generally controls the required performance; the phthalic–maleic anhydride ratio is adjusted to modify the reactivity according to physical properties required for fabrication needs.

Isophthalic Resins

Isophthalic acid (IPA) can be substituted for phthalic anhydride to enhance mechanical and thermal performance and improve resistance to corrosive environments. Significant products include underground gasoline storage tanks and large diameter sewer and water pipe. Although phthalic resins find wide application in ambient fabrication processes, isophthalic resins (Table 2) are more widely used in products employing high temperature forming processes such as pultruded profile and electrical-grade laminate.

Novel polyester compositions have also been derived from dicyclopentadiene [77-73-6] (DCPD), which can enter into two distinct reactions with maleic anhydride to modify properties for lower cost. These compositions have effectively displaced *o*-phthalic resins in marine and bathtub laminating applications.

Recycled poly(ethylene terephthalate) (PET), which offers excellent properties at potentially lower cost, is finding wider use as a raw material component and meeting increasing demands for environmentally compatible resins.

Dicyclopentadiene Resins

These resins, introduced commercially in 1980, have largely displaced *ortho*-phthalic resins in marine applications because of beneficial shrinkage properties that reduce surface profile. The inherent low viscosity of these polymers also allows for the use of high levels of fillers, such as alumina trihydrate, to extend the resin-enhancing, flame-retardant properties for application in bathtub products.

Bisphenol Resins

Ethoxylated and propoxylated derivatives of bisphenol A form the basis for two distinct resin groups that demonstrate superior thermal and corrosion resistance. The addition product of propylene oxide [75-56-9] and bisphenol A, reacted with fumaric acid and dissolved in styrene monomer, has established commercial significance in applications involving extreme corrosive environments.

Table 3.2 Classification of C_5 hydrocarbon resins

Resin type	Softening point, °C R & B	Color, Gardner
Unmodified		
General purpose	100	5–7
Improved	95	5–7
Premium	80–100	3.5–5
Modified		
Cyclic-modified	115	5
Aromatic-modified	liquid to 90	5-9
Cyclic/aromatic-modified	95	3

3.4 Dicyclopentadiene Resins

As already discussed in Section 2.2.3, CPD/DCPD resins are manufactured from steam-cracking by-product streams containing substantial amounts of dicyclopentadiene. The DCPD content of the stream is the basis for the cycloaliphatic structures predominant in this group of resins. The balance of the unsaturates in the starting material are codimers of cyclopentadiene, together with other dienes.

In contrast to the catalytic polymerization type described previously, polymerization of DCPD streams is thermal in character.

Dicyclopentadiene streams containing at least ca. 35 % of dicyclopentadiene respond well to thermal polymerization. Initiated by heating, the reaction is very exothermic, and the temperature must be carefully controlled.

Addition of aromatic unsaturated material, such as styrene, α-methylstyrene, vinyltoluene, or aromatic fractions is usual. Their presence reduces the heat of reaction, and allows modification of the properties of the final resins.

It is important to differentiate between two lines of DCPD-based resins:

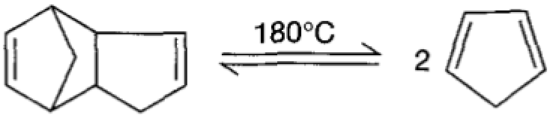
- DCPD resins with a substantial amount of aromatic unsaturated components, It is important to differentiate between two lines of DCPD-based resins:

- DCPD resins with a substantial amount of aromatic unsaturated components, representing an intermediate type with medium bromine numbers of ca. 55–75, i.e., a higher degree of reactivity compared with standard, hydrocarbon resins having bromine numbers in the range of ca. 10–45
- DCPD resins with a predominance of DCPD, showing higher bromine numbers of ca. 65–100 and even higher, which are distinctly heat- and oleo-reactive.

Resins of the first type can be produced, e.g., when using an α-methylstyrene/vinyltoluene cut from a C_9 resin oil as diluent in the polymerization reaction.

The polymerization of DCPD streams is a pressure/temperature (P/T) reaction requiring no catalyst. This P/T reaction may follow the below described scheme:

1) Splitting of DCPD to CPD



On average, a 50–60 % DCPD stream is used in making DCPD resins. When using highly concentrated DCPD fractions as starting material, the P/T reaction has to be carried out in the presence of an aromatic or aliphatic solvent as diluent. It is of advantage to select solvents having a relatively high flash point as they lead to a low solvent viscosity of the resin solution and to a low reaction pressure for the P/T polymerization. Amongst others, xylene, naphtha, mineral spirits 140/160, and similar materials are used.

Polymerization temperature and reaction time have to be matched to each other to facilitate splitting of DCPD to CPD and the subsequent resinification process, and to avoid subsequent crosslinking, which may occur owing to the reactivity of the DCPD resin at elevated temperatures, leading to unwanted insoluble products. Strict monitoring of the temperature is, therefore, absolutely necessary. In this context, the evolution of heat (heat of transformation) is of great importance in the P/T polymerization. At the average manufacturing conditions, the heat of polymerization is in the range 200–300 kJ per kilogram of starting material (e.g., 60 % DCPD in xylene).

A typical example of DCPD resin manufacture (Fig. 3.8) is as follows: After blending the DCPD stream with a diluent if required, manufacture, executed in pressure equipment, usually starts with preheating the starting material to ca. 50–60 °C. The actual polymerization process is executed by increasing the temperature in two or three steps. A certain tion process is executed by increasing the temperature in two or three steps. A certain holding time at the different temperature stages is effected, with the pressure automatically increasing in line with the increasing temperature. The end temperature must not exceed 280 °C. Exact temperature control, especially between 200 and 280 °C, is highly important to prevent subsequent reaction of the polymerizate, e.g., too high a temperature may lead to decomposition of the reaction mixture (explosion). Heating and holding time may vary widely, depending on specific plant and processing conditions, but nevertheless the figures quoted give a rough idea of the system.

The resulting softening points depend on the polymerization conditions, but also on the conditions of the distillation and stripping stages later in the process.

After completion of the polymerization, taking in total ca. 15–17 h, the charge is depressurized, and the material passed to the subsequent distillation and steam-stripping facilities for further processing. Instead of the discontinuous steam-stripping process a continuously operated thin-layer evaporator can also be used. The very mild operating conditions of this method reduce thermal stress on the resin.

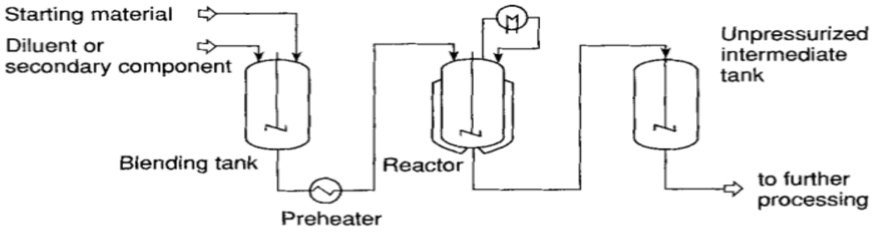


Figure 3.8 Manufacture of DCPD resins

The color of the final resin is subject to thermal stress during the entire manufacturing process, and depends in particular on the level of peroxidation of the starting material. Apart from the general polymerization conditions, it is the variation of the distillation/evaporation conditions (vacuum, evaporation temperature, stripping steam temperature, stripping time) which broadly determine the softening point. By recycling the distillate, it is possible to increase the overall yield of resins considerably.

The cycloaliphatic, unsaturated resin types manufactured in the above described process comprise resins with softening points of 30 to 120°C R & B, Gardner colors 5 to 6, and iodine numbers ranging from ca. 95 to 175.

3.5 Modified Resins

Use of the term "modified" resin is somewhat arbitrary; it is often used to distinguish resins made from straight distillation runs from those based on:

- Streams modified by blending with distinct monomers or fractions
- Streams modified by subsequent reaction of the finished resins, e.g., hydrogenation, or reaction with other reactive compounds, e.g., maleic anhydride

Physical mixtures of resins, e.g., hydrocarbon resins with rosin or rosin derivatives are also on the market and may be classified as modified resins (blended resins).

In view of the wide modification possibilities, only a general summary can be given in the following, illustrated by a few specific examples.

3.5.1 In Situ Modification

The resin profile may be adapted to specific applications by copolymerization of the initial feedstream with other unsaturated monomers, concentrates or fractions. By adding styrene to the indene–coumarone fraction, the penetration depth is improved – a desirable property in resins for floor tiles. By mixing indene concentrates or dicyclopentadiene fractions with C_9 streams, resins with high softening points, useful for ink manufacture, may be produced. Introduction of aliphatic properties in aromatic resins is obtained by polymerization of mixtures of C_9 streams with isobutene, C_5 concentrates, or terpenes. Such resins have improved solubility and compatibility characteristics, useful e.g., in adhesives and rubbers. By addition of phenol to C_9 feedstock, resins with a certain hydroxyl content, compatible with epoxy and polyurethane resins, can be manufactured. Aliphatic feedstreams, particularly piperylene concentrates, may be modified by addition of monoolefins, such as methylbutenes, isobutene, styrene, and α-methylstyrene, leading to resins with lower unsaturation, better stability and color. Tackifying properties may also be improved. Other modifying agents are terpenes, such as α-pinene, β-pinene, and limonene, sometimes used together with aromatic monomers, such as styrene and α-methylstyrene. The resulting resins exhibit high tackifying properties.

DCPD streams, when modified with aromatic olefins or streams containing them, yield resins with high softening points and good solubility. The following examples are an arbitrary choice and serve only as illustrations.