

CHAPTER II

THEORY

This chapter will be focused on laying theoretical ground work to be employed as a basis for interpretation of the experimental results. The general information of poly(ethylene terephthalate) and unsaturated polyesters are stated in section 2.1 and section 2.2 , respectively.

2.1 POLY(ETHYLENE TEREPHTHALATE) [1]

Several polyesters were investigated by Carothers of E.I. du Pont de Nemours and Co.(USA) during a programme of fundamental researches into polymerization which was begun in 1929. These polyesters were mostly linear aliphatic polymers and they generally had low melting points, considerable solubility in organic liquids and poor resistance to hydrolysis. The materials therefore lacked promise as textile fibres and were soon overshadowed by the outstandingly successful polyamide, nylon 6,6. In 1941 Whinfield and Dickson of the Calico Printers Association Ltd.(UK) prepared the aromatic polyester, poly(ethylene terephthalate) and found it to have great promise as a fibre- and film-forming material. Poly(ethylene terephthalate) has since become a major textile fibre. To a lesser extent, the polymer finds application in film form and as a moulding material.

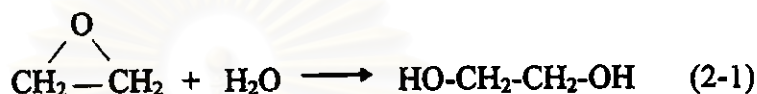
2.1.1 Raw Material

Poly(ethylene terephthalate) may be obtained from ethylene glycol and either terephthalic acid or its ester, dimethyl terephthalate. Until the mid-1960s, all poly(ethylene terephthalate) was produced from the ester, mainly because the acid then available was difficult to obtain with sufficiently high purity whereas the ester was

readily. This situation changed with the advent of fibre-grade terephthalic acid and at the present time approximately equal amounts of the polymer are made from acid and ester.

a) Ethylene glycol

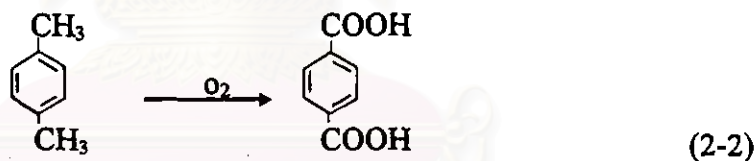
Ethylene glycol is prepared by the hydration of ethylene oxide



Ethylene glycol is a colourless liquid, b.p. 197 °C.

b) Terephthalic acid

The major commercial route to terephthalic acid which is suitable for the direct preparation of poly(ethylene terephthalate) is from p-xylene:

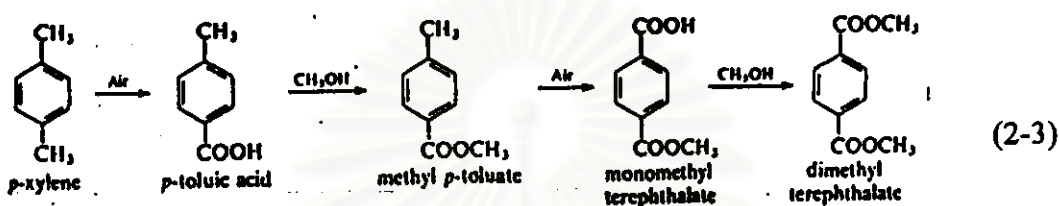


p-xylene is obtained largely from petroleum sources, being a product of the fractionation of reformed naphthas. The oxidation is carried out in the liquid phase. Typically, air is passed into a solution of p-xylene in acetic acid at about 200 °C and 2 Mpa (20 atmospheres) in the presence of a catalyst system containing cobalt and manganese salts and a source of bromide ions. The terephthalic acid produced contains only small amounts of impurities (mainly p-carboxybenzaldehyde), which are readily removed. The acid is dissolved in water at about 250 °C and 5 MPa (50 atmospheres) and treated with hydrogen (which converts the aldehyde to p-toluic acid). The solution is then cooled to 100 °C and pure terephthalic acid crystallizes.

Terephthalic acid is a white solid which sublimes at 300 °C

c) Dimethyl terephthalate

several processes have been developed for the preparation of dimethyl terephthalate from p-xylene, but the most important proceeds as follows:



The oxidation steps are carried out in the liquid phase at 170 °C and 1.5 MPa (15 atmospheres) in the presence of a cobalt acetate or naphthenate catalyst whilst the esterifications are conducted at about 150 °C.

Dimethyl terephthalate may also be produced by esterification of terephthalic acid.

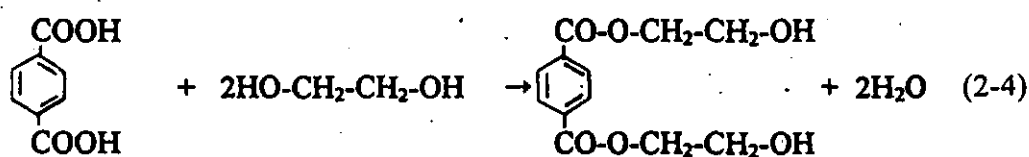
Dimethyl terephthalate is a white solid, m.p. 142 °C.

2.1.2 Preparation

2.1.2.1 Polymerization

As indicated above, poly(ethylene terephthalate) may be prepared from terephthalic acid or dimethyl terephthalate. With both starting materials, the polymerization is carried out in two steps.

In the acid-based process, the initial step is esterification to give mainly bis(2-hydroxyethyl)terephthalate:

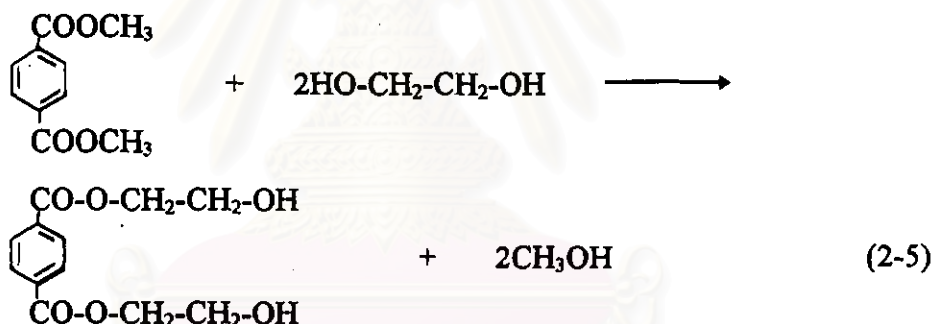


In addition to bis(2-hydroxyethyl)terephthalate, oligomers up to about the hexamer are formed; these have the general formula shown below:



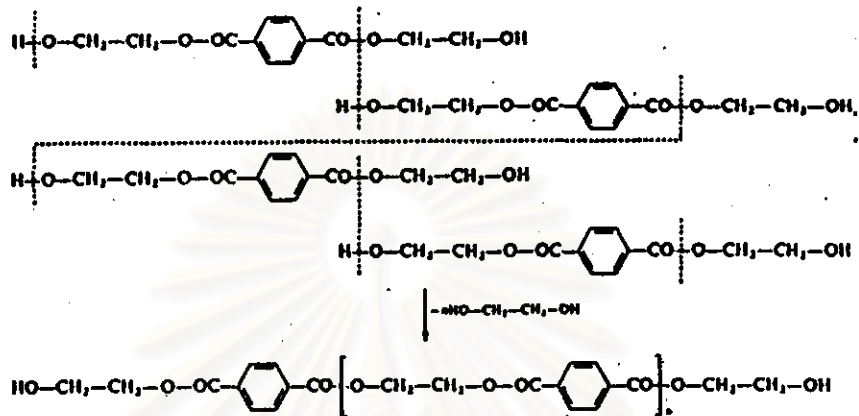
Typically, terephthalic acid is treated with an excess of ethylene glycol (1:1.5 molar) at about 250 °C and 0.4 Mpa (4 atmospheres) and water is allowed to escape as vapour as reaction proceeds.

In the ester-based process, the initial step is ester interchange and again the principal product is bis(2-hydroxyethyl)terephthalate:



Also, some oligomers are formed. In a typical process, dimethyl terephthalate is heated with an excess of ethylene glycol (1:2.2 molar) at 140-220 °C and atmospheric pressure in the presence of a catalyst (usually manganese acetate). Methanol is removed as reaction proceeds.

Whether the starting material is terephthalic acid or dimethyl terephthalate, the second step in the polymerization sequence is the same. An ester interchange reaction occurs, in which the bis(2-hydroxyethyl)terephthalate serves as both ester and alcohol. Successive interchanges result in the formation of a polyester, as represented in the following scheme:



Under the reaction conditions employed, the ethylene glycol which is eliminated is removed continuously from the system; thus there is a progressive increase in molecular weight. Of course, ester interchange reactions also occur at non-terminal ester linkages, but such reactions do not lead to the formation of ethylene glycol and so do not change the average molecular weight of the mixture.

The bis(2-hydroxyethyl)terephthalate is heated at about 290 °C in the presence of a catalyst such as antimony trioxide while the pressure is lowered to about 0.1 kPa (1 mmHg). Ethylene glycol is distilled off as reaction proceeds. Polymerization is continued until the molecular weight reaches the desired level (20000 for fibre and film; 30000 for moulding material).

Compared to the ester-based process, the acid-based process avoids costs involved in using and recycling methanol and gives higher yields. On the other hand, the ester-based process is somewhat easier to carry out.

Figure 2-1 represents a commercial process for this polymerization

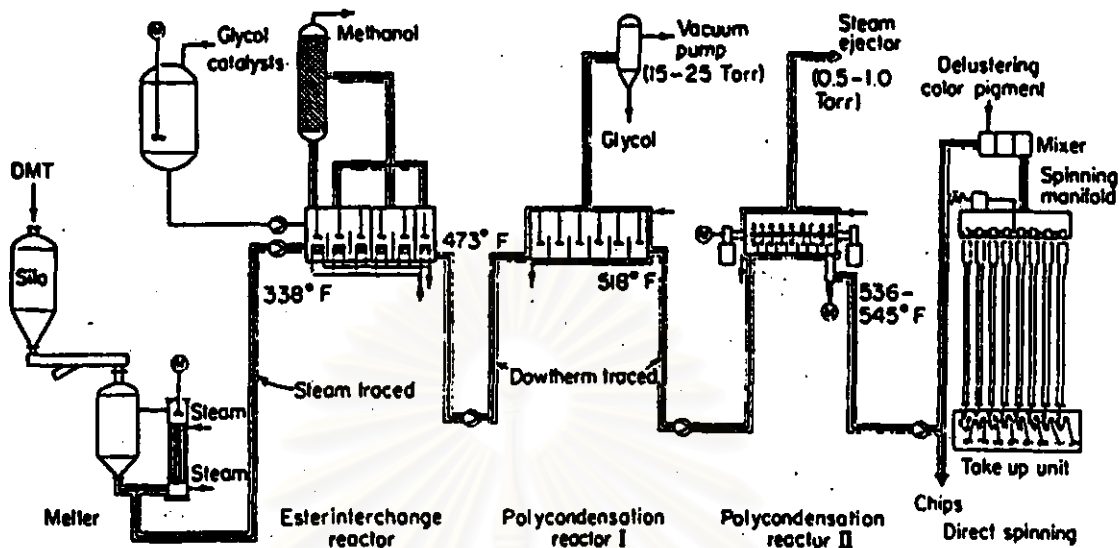
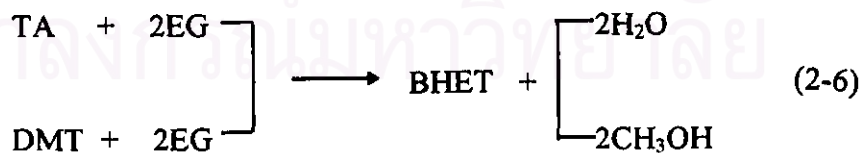


Figure 2-1 Schematic representation of industrial process for synthesis of poly(ethylene terephthalate)[4]

2.1.2.2 Depolymerization

Poly(ethylene terephthalate) is commonly synthesized either by reacting terephthalic acid(TA) and ethylene glycol(EG), or dimethyl terephthalate(DMT) and EG, in the molar ratio of 1:2.0 to 1:2.5. Both polymerization schemes first form the monomer, bis(2-hydroxyethyl)terephthalate (BHET), which then polymerized through polycondensation by releasing EG:



The polycondensation reaction is facilitated by a number of tranesterification catalysts, such as various metal acetates or antimony oxide. The

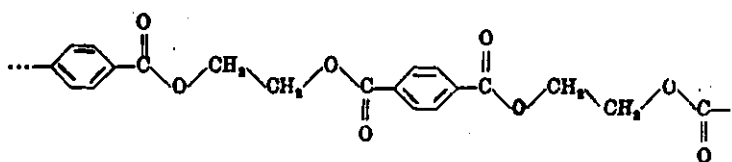
molecular weight of PET is raised to any desired level by evacuating the EG vis solid-state polymerization in the second stage of the process. On the other hand, reversible reaction (2-9) can be preferentially shifted to the left by dissolving PET in excess EG.

Depolymerization of PET by glycolysis in an excess diol, such as ethylene glycol, propylene glycol, and diethylene glycol, has been studied for many years. Most of these studies are proprietary, related to industrial production of polyols and unsaturated polyesters, and are only revealed in a few patents. Vaidya and Nadkarni reported the preparation of unsaturated polyester using the products of PET waste glycolized by propylene glycol in the presence of zinc acetate as catalyst. They showed that the glycolized product consisted mostly of hydroxy terminated monomer, dimer, and trimer, and that the extent of depolymerization increased with increasing amounts of propylene glycol. Later on, they repeated the glycolysis study using EG. Their results showed that in excess EG, the glycolized products contained predominantly BHET [2].

2.1.3 Properties [5]

As a result of the application of various method of investigation, it is possible to represent the structure of poly(ethylene terephthalate) in the following way:

Poly(ethylene terephthalate) consists of a mixture of crystalline and amorphous regions the relative proportions of which depend on the method of preparation. The molecule has an extended rectilinear shape, the plane of the benzene rings being parallel to the plane. The -COO- group is out of the plane of the benzene rings by 12° and the ethylene glycol residue by 20° . Ward has shown that in crystalline poly(ethylene terephthalate) the group -OCH₂-CH₂O-, has the *trans*- configuration[5]:



Physical properties

Ordinary poly(ethylene terephthalate) has a specific gravity (sp.gr.) of 1.38. It is a polymer which contains a considerable amount of crystalline fraction. However, on rapidly cooling molten poly(ethylene terephthalate) it can be obtained completely amorphous in the form of perfectly transparent samples with a sp.gr. of 1.33. The specific gravity of the completely crystalline fraction is 1.455.

The transparent modification of poly(ethylene terephthalate) is stable up to 80 °C. Above this temperature, transformation of the amorphous fraction to the crystalline begins and the sample becomes cloudy. The glass point lies between 80 and 90 °C.

poly(ethylene terephthalate) is a non-hydrophilic substance. On immersion in water at 25 °C for a week, it absorbs less than 0.5 percent of water. Its mechanical properties remain virtually unchanged. The wettability of poly(ethylene terephthalate) has been investigated and it has been found that it is wetted by liquids which form hydrogen bonds better than polystyrene and polyethylene are. The physical properties of poly(ethylene terephthalate) are given in Table 2-1.

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Table 2-1 The general properties of poly(ethylene terephthalate) [5]

Properties	Numerical magnitude
specific gravity	1.38
specific gravity(amorphous)	1.33
specific gravity(crystalline)	1.455
Absorption of water on immersion in water at 25 °C for one week,%by weight	0.5
Refractive index for light :at 25 °C	1.574
Refractive index for light :at 2 °C	2.48

Thermal properties

The melting point of poly(ethylene terephthalate) lies within the range 250-265 °C. Zero strength for poly(ethylene terephthalate) is at 248 °C (zero strength denotes the temperature at which a film just withstands a load of 1.4 kg/cm² for 5 sec). The rest of the thermal characteristics are given in Table 2-2.

Mechanical properties

Poly(ethylene terephthalate) in the form of a film, fibre or massive objects possesses a high strength. In Table 2-3 are given mechanical properties of poly(ethylene terephthalate) and Table 2-4 are given comparative data for films of poly(ethylene terephthalate), polyethylene(PE), cellulose acetate and cellophane.

The mechanical properties of a poly(ethylene terephthalate) film change little over the temperature interval from -20 to +80 °C. No brittleness is observed even at -60 °C.

Table 2-2 The thermal properties of poly(ethylene terephthalate) [5]

Properties	Numerical magnitude
Melting point, °C	265
Glass point, °C	80-90
Zero strength, °C	248
Specific heat, cal/g-degree at 25 °C	0.315
Specific heat, cal/g-degree at 200 °C	0.476
Thermal conductivity, cal/cm.sec.degree	3.63×10^{-4}
Latent heat of fusion, cal/g	11-16
Inflammability	ignites and burns with difficulty
Resistance to cold	remains elastic to -50 °C

Table 2-3 Mechanical properties of poly(ethylene terephthalate)[5]

Properties	Numerical magnitude
Yield stress, kg/cm ²	980
Tensile strength at break, kg/cm ²	1750
Resistance to repeated flexing	no appreciable effect after 100,000 cycles
Elongation at break, %	50-70
Resistance to breaking, kg/mm ²	50-70
Impact strength, kg-cm	90
Tensile modulus, kg/cm ²	35,200

Table 2-4 Comparative mechanical properties of films (25 °C, 35% relative humidity)[5]

Properties of the polymer	PET	Polyethylene	cellulose acetate	cellophone
Thickness, mm.	0.0254	0.0381	0.0223	0.0254
Tensile strength, kg/cm ²	1638.2	168.7	633.0	563.0
Elongation, %	70	700	20	30
Tensile modulus, kg/cm ²	35,200	1336	24,610	28,100
Tear strength, g	18	175	4	5
Impact strength, kg-cm	90	15	10	15
Flex, cycles	20,000	26,000	300	600

Permeability

Poly(ethylene terephthalate) film is almost impermeable to water vapour and the vapours of organic solvents. Table 2-5 are given permeability of a Poly(ethylene terephthalate) film.

Poly(ethylene terephthalate) film is almost impermeable to such gases as oxygen and nitrogen. Films with a thickness of 0.5 mil at 100 percent relative humidity pass oxygen to the amount of 5.7 g/100 m².hr and nitrogen to the amount of 5.2 g/100 m².hr.

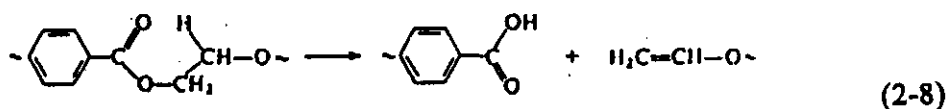
Table 2-5 Permeability of a poly(ethylene terephthalate) film (thickness 1 mil) for vapours of solvents[5]

Solvents	Permeability g/100 m ² .hr
Water (at 39.5 °C)	160
Ethyl alcohol	0
Ethyl acetate	4
Carbon tetrachloride	7
Hexane	6
Benzene	18
Acetone	82
Acetic acid	0

Resistance to the action of chemical reagents

Poly(ethylene terephthalate) is unaffected at room temperature and even at a temperature close to the boiling point under the action of such solvents as ethyl acetate, acetone, xylene, dioxan, trichloroethane and glacial acetic acid. Acids act more weakly than alkalines. The latter on prolonged action decompose the polyester. A strong solution of ammonia has a particularly powerful action. Nitric acid also decomposes it. Phenols dissolve poly(ethylene terephthalate). Strong sulphuric acid simultaneously dissolves and decomposes it. Table 2-6 shows the stability of poly(ethylene terephthalate) to the action of chemical and other agents.

The resistance of poly(ethylene terephthalate) to photochemical degradation is very good. Some thermal degradation occurs when the polymer is heated above the melting point, the principal products being carbon dioxide, acetaldehyde and terephthalic acid. The following molecular reaction is involved[1]:



Carbon dioxide may arise by decarboxylation of the carboxylic acid whilst acetaldehyde may be formed by cleavage of the vinyl ether group through ester interchange.[1]

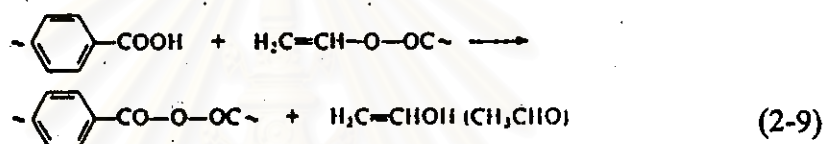


Table 2-6 Stability to the action of chemical and other reagents[5]

Reagents	Stability
Boiling water	no effect
Phosphoric acid	no effect
Sulphuric acid	dissolves
Alkalies	moderate
Sodiumhydrosulphite	stable
Oxidizing agents	stable
Organic liquids	stable
Phenols	dissolves
Chlorinated phenols	dissolves
Resistance to the action of moths and micro-organisms	resistant
Resistance to sunlight	resistant
Resistance to ultra-violet light	moderate

2.2 UNSATURATED POLYESTERS

2.2.1 Definitions

Polyesters are condensation products of dihydric or polyhydric alcohols and dibasic or polybasic acids. The term is a broad one, and includes saturated polyesters plasticisers such as poly(propylene adipate), polyester fibre-forming compounds such as poly(ethylene terephthalate), and polyesters modified by fatty acids and drying oils, the alkyds or glyptals used in the paint and varnish industry. By common usage, however, the term polyester when used alone is synonymous with unsaturated polyester resin.

Unsaturated polyesters are the most common polymers used in conjunction with glass fibre reinforcing. They are prepared from difunctional monomers, one of which contains a double bond that is capable of undergoing addition polymerization in a subsequent crosslinking reaction. Most commercially available unsaturated polyester resins are produced by reacting a glycol with an unsaturated dibasic acid which is generally maleic or fumaric acid. The linear chain polymer so formed is then dissolved in a polymerizable monomer, usually styrene, and the resulting resin is called a polyester. This can be cured by the use of catalysts with or without heat to yield a hard insoluble thermoset solid [6].

2.2.2 Development

The modern history of unsaturated polyester resins begins with the filing of a patent application in 1922 by Carleton Ellis, and the subsequent publication of this patent in 1933. This covers the reaction products of dihydric alcohols and dibasic acids or anhydrous for use as lacquers.

Hundreds of publications followed in the succeeding ten years, but the important developments can be traced through several stages. First came the formation of interpolymers of esters of dibasic acids with vinyl compounds by Dykstra in

1934. Then followed the work by Bradley, Kropa, and Johnston, who prepared polymerizable compositions based on maleic anhydride. This was followed by a further publication of Ellis describing the copolymerization of maleic polyester resins with monomeric styrene in the presence of peroxide catalyst.

The commercial development of unsaturated polyester resins began in the United States in 1941, when an allyl casting-resin was introduced for use as a glass substitute. Here unsaturation was obtained by using an unsaturated alcohol, allyl alcohol, instead of following the more usual practice of using an unsaturated acid such as maleic or fumaric. This was followed in 1942 by an allyl low pressure laminating resin, allyl diglycol carbonate, which was used for the manufacture of some of the first glass cloth reinforced resin radomes for aircraft.

By 1946 polyester resins were commercially available in the United States consisting of the polyester of diethylene glycol and maleic anhydride, with styrenes, and similar resins were soon manufactured in this country [6].

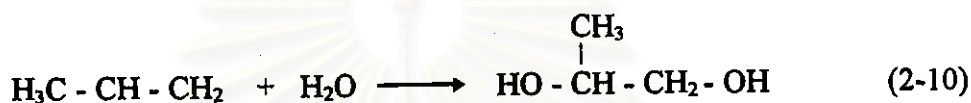
2.2.3 Raw Material [1],[6]

Linear unsaturated polyesters are prepared commercially by the reaction of a saturated diol with a mixture of an unsaturated dibasic acid and a "modifying" dibasic acid (or corresponding anhydrides). In principle, unsaturation desired in a polyester can be derived from either an unsaturated diol or an unsaturated acid; for economic reasons the latter is invariably preferred. As mentioned previously, the unsaturated acid provides sites for subsequent cross-linking; the function of the modifying acid is to reduce the number of reactive unsaturated sites along the polymer and hence to reduce the cross-link intensity and brittleness of the final product. Some acids and anhydrides which are used to modify polyesters are, in fact, unsaturated but the double bonds are not sufficiently reactive to represent sites for subsequent cross-linking.

2.2.3.1 Diols

(a) Propylene glycol

propylene glycol is the diol most widely used for the manufacture of linear unsaturated polyester; it is prepared by the hydration of propylene oxide.



Commonly the reaction is carried out without a catalyst at about 200 °C and 2 MPa (20 atmospheres). Propylene glycol is isolated by distillation under reduced pressure; it is a colourless liquid, b.p. 189 °C. Propylene glycol is the preferred diol because it forms polyesters which are compatible with styrene and which show little tendency to crystallize; it is also readily available at low cost.

(b) Ethylene glycol

Ethylene glycol is the simplest glycol having a symmetrical structure, and is also widely used industrially for making polyester resins (Figure 2-2(a)). Polyesters made with ethylene glycol show a strong tendency to crystallize, and they have a limited compatibility with styrene, sometimes used in admixture with other diols.

(c) Diethylene glycol

Diethylene glycol containing an oxygen linkage (Figure 2-2(b)), also produce non-crystallizing polyesters and leads to greater flexibility although water-sensitivity is increased.

(d) Neopentylene glycol (2,2-dimethyl-1,3-propanediol)

Neopentylene glycol (Figure 2-2(c)) produce polyester that do not have a very high thermal softening point when cured, they show less loss in weight when heated and will withstand higher temperatures before degradation take place.

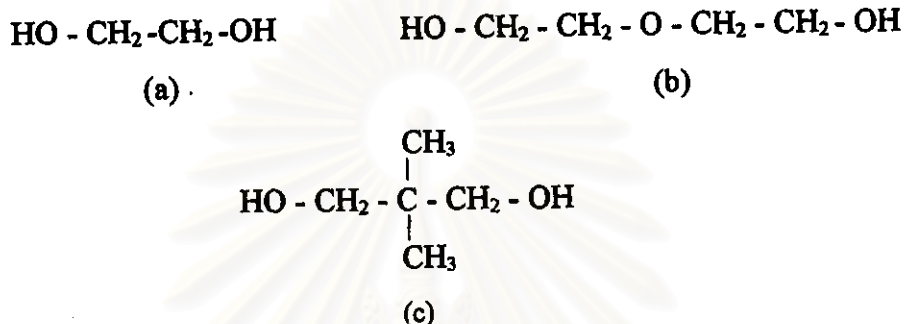
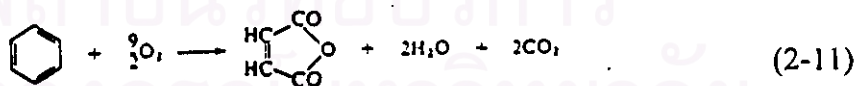


Figure 2-2 Chemical structure of diols ;(a) Ethylene glycol ;
(b) Diethylene glycol ;(c) Neopentylene glycol [1]

2.2.3.2 *Unsaturated acids and anhydrides*

(a) Maleic anhydride

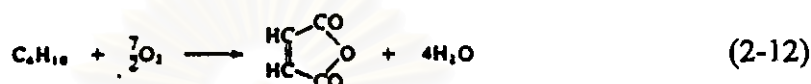
Maleic anhydride is the most important unsaturated component used in the manufacture of linear unsaturated polyesters. It is mostly obtained by the oxidation of benzene:



The reaction is carried out in the vapour phase by passing a mixture of benzene and excess of air over a vanadium pentoxide catalyst at 350-450 °C. The effluent is cooled and most of the maleic anhydride is condensed. The non-condensed material passes to a scrubber where the remaining anhydride is hydrolyzed to maleic acid. The maleic acid solution then passes to evaporators for

concentration and dehydration. High purity anhydride is obtained by distillation under reduced pressure.

Because of a rise in price of benzene, increasing amounts of maleic anhydride are being obtained from cheaper n-butane:



Reaction conditions are similar to those used for the oxidation of benzene. Maleic anhydride is a white crystalline solid, m.p. 52-53 °C. Maleic anhydride is preferred to maleic acid since it is more reactive and give rise to less water on esterification.

(b) Fumaric acid

Fumaric acid (Figure 2-3(a)) is the trans isomer of maleic acid (Figure 2-3(b)), is widely used, and there is plenty of evidence that maleic acid isomerizes almost completely in many reactions with glycols, so that resins based on fumaric acid differ little from those based on maleic anhydride. Fumaric polyesters have a higher thermal softening point when cured, and also show a greater tendency towards crystallization, probably because the trans structure produces a more linear polymer. Fumaric acid is sometimes preferred to maleic anhydride as it is less corrosive and gives lighter-coloured products with slightly improved heat resistance.

(c) Itaconic acid

Itaconic acid (Figure 2-3(c)) can also be used to produce interesting polyesters, but because esters of itaconic acid have a tendency to homopolymerize, the polyesterification should be carried out in the presence of an inhibitor such as hydroquinone. Itaconic polyesters are also unstable unless carefully inhibited.

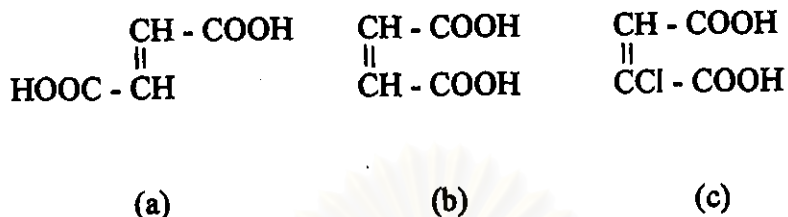
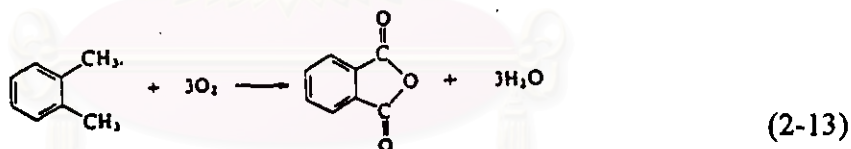


Figure 2-3 Chemical structure of unsaturated acid ;(a) Fumaric acid; (b) Maleic acid; (c) Itaconic acid. [1]

2.2.3.3 *Modifying acids and anhydrides*

(a) Phthalic anhydride

The most important modifying component used in the manufacture of linear unsaturated polyesters is phthalic anhydride. The anhydride is generally obtained by the oxidation of o-xylene:



The reaction is carried out in the vapour phase by passing a mixture of o-xylene and air over a catalyst such as vanadium pentoxide supported on silica and promoted with titanium dioxide at about 400 °C. The exit gases are cooled and the phthalic anhydride is collected and purified by distillation under reduced pressure.

Older processes based on the air-oxidation of naphthalene (obtained from coal) are now of minor importance.

Phthalic anhydride is a white crystalline solid, m.p. 131 °C. Phthalic anhydride gives polyesters which are compatible with styrene and the cross-linked products are hard and rigid.

(b) Sebacic and adipic acids

Sebacic and adipic acids have been widely used for producing flexible polyesters.

(c) Isophthalic acid

Isophthalic acid is the m-isomer of phthalic acid (Figure 2-4(a)), can be used in place of the latter, in which case the polyester will have a higher viscosity when condensed to the same degree. Cured isophthalic polyesters are characterized by being tougher, and having a lower volatile loss when heated, than phthalic resin.

(d) Endomethylenetetrahydrophthalic anhydride

The Diels-Alder reaction product of cyclopentadiene and maleic anhydride (Figure 2-4(b)). Resin based on this acid or anhydride have a considerably higher thermal softening point than those based on phthalic anhydride, as well as a lower volatile loss. They are suitable therefore for applications requiring moderate heat resistance.

(e) Tetrachlorophthalic anhydride

Tetrachlorophthalic anhydride is also used industrially in polyester resins for conferring a small measure of flame resistance (Figure 2-4(c))

(f) Chlorendic acid (HET acid)

Chlorendic acid is prepared by the Diels-Alder reaction of hexachlorocyclopentadiene and maleic anhydride; the initial product is "chlorendic anhydride" but this rapidly absorbs water from the air to give the acid (Figure 2-4(d))

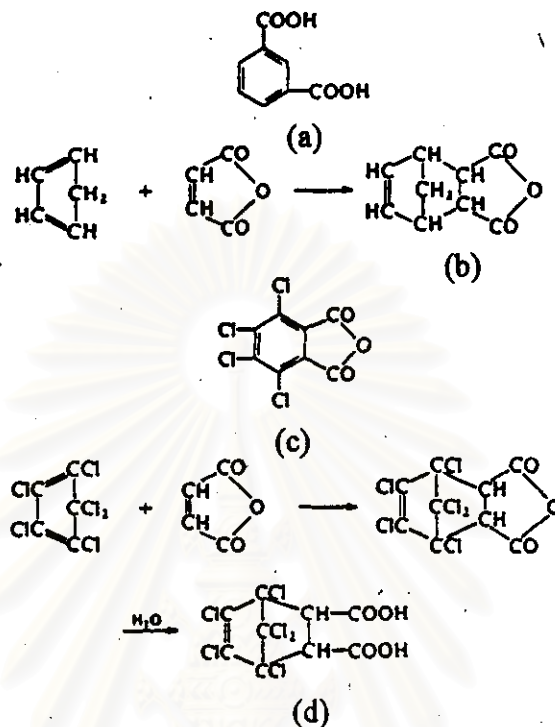


Figure 2-4 Chemical structure of modifying acid and anhydrides;

- (a) Isophthalic acid; (b) Endomethylenetetrahydrophthalic anhydride; (c) Tetrachlorophthalic anhydride; (d) chlorendic acid. [1]

2.2.3.4 Cross-linking monomer

It is possible to cross-link unsaturated linear polyester chains directly one to another; however, reaction is slow and a low degree of cross-linking is achieved. These limitations are overcome by the introduction of a material which forms bridges between the chains. The material most commonly used to cross-link unsaturated linear polyesters in this way are vinyl monomers. The addition of a liquid vinyl monomer to the polymer also leads to a reduction in viscosity and this facilitates the impregnation of glass-fibre in the preparation of laminates.

(a) Styrene

Styrene (Figure 2-5(a)) readily copolymerizes with maleic polyesters; it has a low viscosity, and is freely available at a low price. For these reasons styrene is very widely used in industrial polyester resins. Resins based on styrene cure rapidly and have good weathering characteristics.

(b) Diallyl phthalate

Diallyl phthalate (Figure 2-5(b)) has been used with polyester since about 1946. Polyesters modified with diallyl phthalate in place of styrene are tougher when cured, and they have a higher thermal softening point. This is due to the tetrafunctionality of diallyl phthalate, which increase the degree of cross-linking.

(c) Triallyl cyanurate

Triallyl cyanurate (Figure 2-5(c)) are used for heat resistance polyesters.

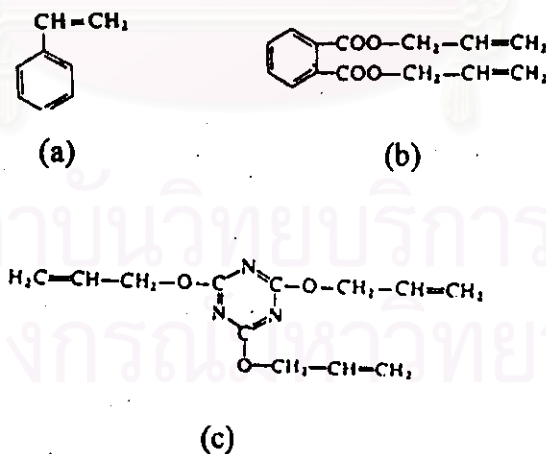


Figure 2-5 Chemical structure of cross-linking monomer

(a) styrene; (b) diallyl phthalate; (c) triallyl cyanurate [1]

2.2.3.5 *Initiators and inhibitors*

As has been noted previously, the cross-linking of unsaturated linear polyesters involves the reaction of the unsaturated sites in the polymer chain with a vinyl-type monomer. This reaction is analogous to conventional vinyl copolymerization and proceeds by an essentially similar mechanism. As carried out in commercial practice, cross-linking of unsaturated polyesters is invariably a free radical reaction. Two types of initiating systems are commonly employed for this reaction, namely those effective at elevated temperatures and those effective at room temperature.

The most important initiators used for unsaturated polyester are as follows:

(a) Peroxides

Some of the foregoing peroxy compounds are peroxides, having the generic formula $R-O-O-R'$, where R and R' may or may not be identical. The most useful peroxide catalyst for polyester resins is benzoyl peroxide.

Benzoyl peroxide (Figure 2-6(a)) is used principally for curing polyester resins at elevated temperature. It is therefore a fairly stable catalyst. Polyester resins containing 2% of benzoyl peroxide (this is a typical catalyst content) remain stable at normal room temperature for upwards of 10 days. Benzoyl peroxide does not dissolve readily in polyester resins in its dry or partially damped powder form. It is normally supplied, therefore, as a catalyst paste consisting of a fine dispersion of benzoyl peroxide in a plasticiser medium such as dibutyl phthalate or tricresyl phosphate.

2,4-Dichlorobenzoyl peroxide (Figure 2-6(b)), which has a slightly lower critical temperature than benzoyl peroxide, is sometimes used as a catalyst in cast polyester resin. It is used in conjunction with a cold-setting catalyst/accelerator system which gels the resin only at room temperature. The soft gel is then heated slowly to above 65 °C when the 2,4-Dichlorobenzoyl peroxide takes over and continues the curing process to completion. In this way fairly large crack-free castings can be made with polyester resins.

Di-t-butyl peroxide (Figure 2-6(c)) is used whenever a long catalyzed resin potlife is needed. It has a critical temperature of 100 °C, but in order to achieve a reasonably rapid cure, a temperature of over 150 °C may be necessary.

Lauroyl peroxide (Figure 2-6(d)) is sometimes used for medium-temperature curing, e.g. 60-70 °C. It has a half-life of only 25 min at 85 °C when measured in an inert solvent.

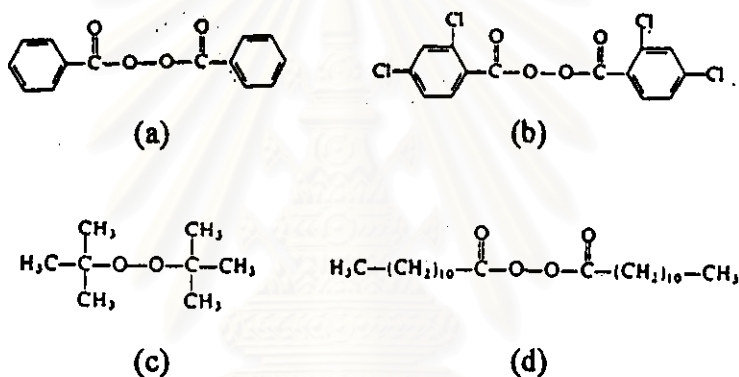


Figure 2-6 Chemical structure of peroxides used as initiator for unsaturated polyester; (a) Benzoyl peroxide; (b) 2,4-Dichlorobenzoyl peroxide; (c) Di-t-butyl peroxide; (d) Lauroyl peroxide [1]

(b) Hydroperoxides

Many compounds having the generic formula R-O-O-H are also suitable as polyester catalysts. These are the hydroperoxides. The simplest is hydrogen peroxide, which is a fairly reactive polyester catalyst once it has been made compatible with the resin by using a suitable solvent.

The two most important catalysts which are now used for cold curing polyester resins are **cyclohexanone peroxide (H.C.H)** and **methyl ethyl ketone peroxide (M.E.K.P)**. The names are rather misleading. Neither of these catalysts is a single simple compound, and they both have a variable composition

depend on their source of manufacture. They are both essentially hydroperoxides, and not peroxides. In addition to this, cyclohexanone peroxide is normally supplied as a 50% paste in either dibutyl phthalate or tricresyl phosphate, and methyl ethyl ketone peroxide is supplied as a solution in dimethyl phthalate.

The reaction between hydrogen peroxide and cyclohexanone yield a number of peroxy compounds, the structure of which were determined by Criegee, Schnorrenberg, and Becke. H.C.H. catalyst is a mixture of at least two of the following compounds, the exact composition depending on the source of manufacture. The principal components of commercial cyclohexanone peroxide shows in Figure 2-7

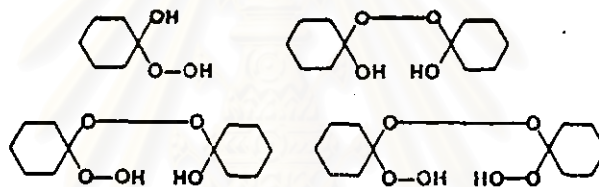


Figure 2-7 The principal components of commercial cyclohexanone peroxide [1].

Methyl ethyl ketone peroxide, M.E.K.P., is also a mixture of several peroxy compounds, and its composition will also vary therefore, depending on the manufacturer. Karnojitzki has suggested that the following main compounds, among others, are present in commercially available M.E.K.P. Figure 2-8 show the main components of commercial methyl ethyl ketone peroxide.

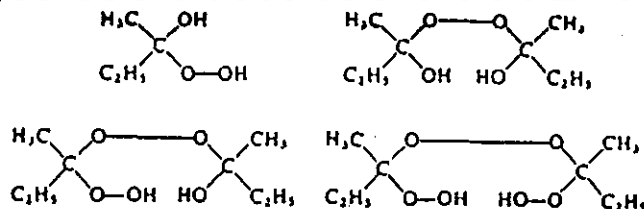


Figure 2-8 The main component of commercial MEKP [1]

t-Butyl hydroperoxide was one of the earliest hydroperoxide catalysts used in polyester resins. It is not so widely used now as formerly, because of its poor stability when compared with either H.C.H. or M.E.K.P.

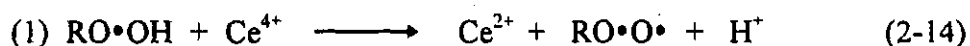
Cumene hydroperoxide is frequently used for hot-curing, often in association with benzoyl peroxide, when it is required to cure at an intermediate temperature (e.g. 70 °C). The benzoyl peroxide starts liberating free radicals at about 70°C, and when the exotherm of the curing resin reaches about 100 °C (the critical temperature of cumene hydroperoxide) this also liberates free radicals and completes the cure.

(c) Effect of metals as accelerators [6]

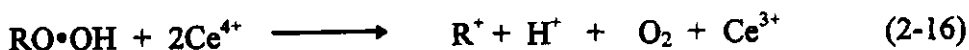
Hydroperoxides can be decomposed at normal temperatures to liberate free radicals by the use of certain metal compounds. In this way it is possible to have a catalyst/accelerator system which will cure a polyester resin without heat.

There are two quite different mechanisms, according to Tobolsky and Mesrobian. In the first a powerful oxidizing agent breaks down the hydroperoxide to produce one equivalent of oxygen for every equivalent of oxidizing agent used. In the second a reducing agent reacts with the hydroperoxide, acting here as an oxidizing agent, so as to produce many moles of oxygen for each mole of hydroperoxide consumed.

Ceric salts and lead tetraacetate supply examples of the first mechanism. The reaction takes the following courses:



Thus the overall reaction is



Most polyester resins are cured at room temperature by using a hydroxide and cobalt naphthenate, an example of the second mechanism. In this reaction the cobaltous cobalt (Co^{2+}) is first oxidized to Co^{3+} , thus:



The cobaltous cobalt is then generated, leading to a chain decomposition of the hydroperoxide:



The cycle is repeated until all the hydroperoxide has been decomposed.

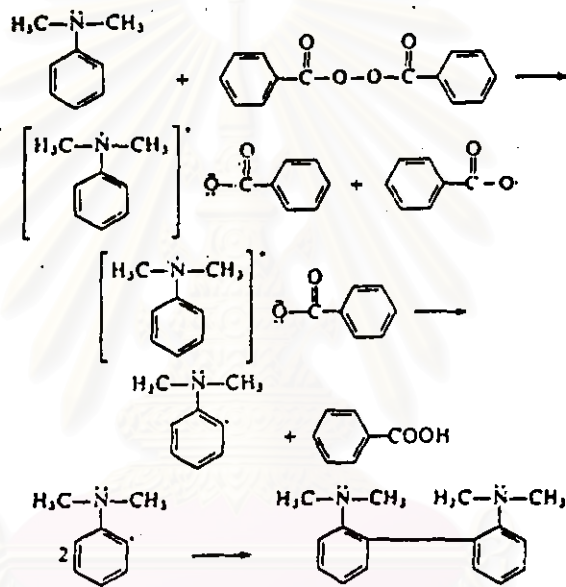
Recently the use of soluble vanadium salts, and in particular vanadium naphthenate, has been used to decompose cumene hydroperoxide in the presence of benzoyl peroxide. This system is sometimes used in the continuous manufacture of glass fibre reinforced polyester sheeting. Alternatively, iron can be employed in the form of the complex dicyclopentadienyl-iron (ferrocene), $\text{Fe}(\text{C}_2\text{H}_5)_2$. This is ideal in conjunction with cumene hydroperoxide when a rapid gel is required at a specific temperature such as 80 °C.

(d) Tertiary amines as accelerators

Whereas the foregoing metal-based accelerators are highly reactive with hydroperoxides, and have little or no reactivity with peroxides, tertiary amines are specific for peroxides. From 1925 onwards, Gambarjan and co-workers studied the reaction of benzoyl peroxide and various amines.

Amines such as dimethylaniline, diethylaniline and dimethyl-*p*-toluidine react violently with benzoyl peroxide and initiating systems based

on these materials have found some use, principally on account of the long-pot life of resin containing either benzoyl peroxide or tertiary amine. On the other hand, polyester resins cured with benzoyl peroxide-tertiary amine tend to discolour and craze on ageing. The reaction between benzoyl peroxide and a tertiary amine is thought to proceed via a one-electron transfer from nitrogen, as shown in the following example involving dimethylaniline[1]:



(e) inhibition

Unsaturated polyester resins are stable at normal room temperature in the absence of a cross-linking agent. As soon as the cross-linking monomer has been incorporated, however, the system is liable to gel at normal temperature in a matter of hours, days, or weeks depending on the degree of unsaturation present. Since the high viscosity of many polyester resins at room temperature often necessitates blending the resin with the cross-linking monomer at

elevated temperatures, gelation can occur immediately the hot polyester first comes into contact with the monomer. It is, therefore necessary to incorporate inhibitors in polyester resins.

Typical inhibitors of free radical chain reactions fall into the following classes:

Inorganic substances: sulphur, copper, nitrates.

Polyhydric phenols : hydroquinone, catechol, t-butylcatechol, pyrogallo

Quinones: naphthaquinone, 1,4-benzoquinone, phenanthraquinone.

Aromatic nitro compounds: dinitrobenzene, trinitrotoluene picric acid

Amines: pyridine, N-phenyl- β -naphthylamine

Most commercial polyester resins are inhibited with small amounts (e.g. about 0.02%) of hydroquinone, t-butylcatechol, benzoquinone, or dihydroxydiphenyl, or combinations of these inhibitors. In the presence of these inhibitors most polyester resins will remain stable at normal room temperature (20 °C) in the dark for six months to six years. As soon, however, as a catalyst, or a catalyst/accelerator system, is added, cross-linking takes place readily and the resin can be cured.

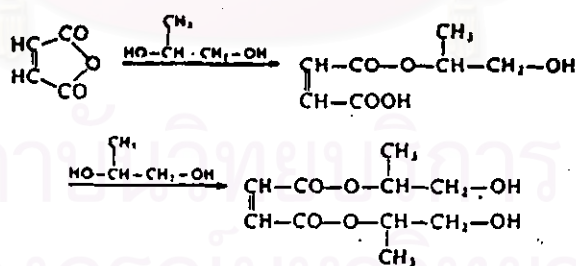
2.2.4 Preparation [1]

Linear unsaturated polyesters are prepared batch-wise by heating a mixture of the appropriate acidic and hydroxy components in a reactor jacketed for heating and cooling and fitted for distillation. A typical formulation for a general purpose material might be as follows:

Propylene glycol	100	parts by weight
Maleic anhydride	72	
Phthalic anhydride	54	

The molar ratio of the ingredients shown above is 1.2 : 0.67 : 0.33; the excess of glycol is to allow for loss during the reaction and to restrict the molecular weight of the polymer. The mixture is heated at 150-200 °C for 6-16 hours and water is continuously distilled from the reactor. Sometimes xylene is added to the reaction mixture to assist in the removal of water by azeotropic distillation and sometimes a catalyst such as p-toluenesulphonic acid is added to reduce the reaction time. In order to prevent discoloration, the reaction is carried out in an inert atmosphere of either carbon dioxide or nitrogen. Heating is continued until the average molecular weight of the polyester reaches about 1000-2000. The polymer is then cooled to about 90 °C and pumped into a blending tank containing vinyl monomer to which has been added an inhibitor such as hydroquinone. In a general purpose material, the weight of styrene used is about half that of the polymer. The blend (which is commonly referred to as "polyester resin") is then allowed to cool to room temperature

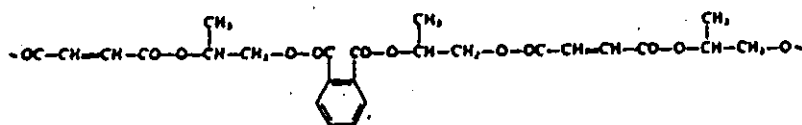
The reaction between a hydroxy-compound and an anhydride proceeds in two distinct steps. In the first step, esterification of the anhydride occurs to form a free acid group which is then esterified in the second step, e.g.



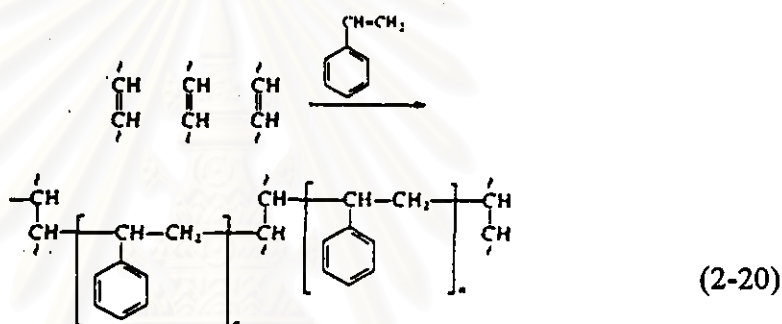
(2-19)

The first step proceeds more rapidly than the second since the anhydride group is more reactive than the free acid group. Clearly, a diol and an anhydride may interact through a sequence of reactions of the foregoing type to yield a

linear polyester. Thus a segment of the polyester obtained from propylene glycol, maleic anhydride and phthalic anhydride might have the following structure:



The cross-linking of an unsaturated linear polyester by means of a vinyl monomer such as styrene may be represented as shown:



2.2.6 Properties of cured unsaturated polyesters

The cured properties of unsaturated polyesters vary in importance depending on the use the cured material is being put to. The main properties of interest from an application standpoint fall into the following categories:

- (1) Physical properties: mechanical properties, physical constants.
- (2) Electrical properties
- (3) Chemical properties

Physical properties

The standard physical properties usually reported for cast polyester resins include all the standard mechanical strength properties commonly

determined on plastic materials. These properties are generally run in accordance with the procedures found in "ASTM standard for plastics" or in accordance with procedures recognized by other national or international agencies or standard groups. In addition to data from these mechanical tests, certain other physical constants (such as hardness, specific gravity, refractive index, thermal coefficient of expansion, etc.) are generally useful in characterizing resins. The ranges of physical properties generally covered by polyester resins are listed in Table 2-8

Table 2-7 Physical properties of cured unsaturated polyester resins [7]

	ASTM Test Method	Polyester cast resins	
		Rigid	Flexible
Flexural strength, psi	D790	8,500-18,300	-
Tensile strength, psi	D683, D651	6,000-10,000	800-1800
Tensile modulus, psi x 10 ⁵	D638	3.0-6.4	-
Tensile elongation, %	D638	< 5	40-310
Compressive strength, psi	D695	13,000-36,500	-
Impact strength	D256	0.2-0.4	7.0
Heat distortion temperature, °F	D648	140-400	-
Hardness, Rockwell	D785	M70-115	-
Barcol		20-60	-
Shore		-	84-94
Specific gravity	D792	1.10-1.46	1.01-1.20
Refractive index	D542	1.523-1.57	1.537-1.55
Thermal expansion, 10 ⁻⁵ /°C	D696	5.5-10	-
Resistance to heat, °F	-	250	250

Electrical properties

The electrical properties of polyester resins are considered to be very good in comparison with other dielectric materials. Table 2-9 lists the ranges in electrical properties which are available in standard polyester resins.

Table 2-8 Electrical properties of cured unsaturated polyester resins [7]

	ASTM Test Method	Polyester cast resins	
		Rigid	Flexible
Volume resistivity ¹	D257	10 ¹⁴	10 ¹⁴
Dielectric strength ²	D149	380-500	250-400
Dielectric strength ³	D149	280-420	170
Dielectric constant	D150		
60 cycles		3.0-4.36	4.4-8.1
10 ³ cycles		2.8-5.2	4.5-7.1
10 ⁶ cycles		2.8-4.1	4.1-5.9
Dissipation (power) factor	D150		
60 cycles		0.003-0.028	0.026-0.31
10 ³ cycles		0.005-0.025	0.016-0.05
10 ⁶ cycles		0.006-0.026	0.023-0.06
Arc resistance, sec.	D495	125	125

Chemical resistance

Although there is an endless variety of unsaturated polyester compositions on the market, the majority of so-called general-purpose polyester resins have a similar degree of resistance to standard chemical reagents as used in such tests as ASTM D543-52. By careful selection of components and manufacturing procedures, polyester resins with a somewhat higher degree of chemical resistance can be

prepared. The specific chemical resistance of a completely cured polyester resin is a function of its chemical composition, molecular weight of the polyester backbone, degree of cross-linking, type of monomer and other factors.

The general resistance of polyester resins compared with other groups of plastic is shown in Table 2-10. Based on their fair to good chemical resistance characteristics and ease of fabrication into structural parts, reinforced polyester resins are one of the best non-metallic structural materials which can be used for tanks, ducts, fume hoods, pipe, etc., where a combination of chemical resistance and strength is required.



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Table 2-9 General chemical resistance of polyester resins on a comparative basis [7]

Plastic material	Chemical Exposure				
	General	Reducing conditions-acid	Oxidizing conditions-acid	Alkaline	Solvents
Polyester	Fair	Fair	Good	Poor	Fair
Acrylic	Poor	Fair	Poor	Fair	Poor
cellulose ester	Poor	Poor	Poor	Poor	Poor
Epoxy	Fair	Fair	Poor	Good	Excellent
Fluorocarbon	Excellent	Excellent	Excellent	Excellent	Excellent
Furan	Good(filled)	Good(filled)	Poor	Good(filled)	Good
Nylon	Poor	Poor	Poor	Poor	---
Phenolic	Good(filled)	Good(filled)	Poor	Poor(filled)	Good
Polyethylene	Good	Good	Fair	Good	Good
Polyvinyl alcohol	Poor	---	---	---	Excellent
Saran	Good	Good	Good	Fair	Good
Styrene	Fair	Fair	Fair	Fair	Fair
Vinyl	Good	Good	Good	Good	Fair