1.1 POLYESTER RESINS

Polymers are substances whose molecules consist of a large number of units of a few types: the units themselves, consisting of a number of atoms, are usually referred to as the segments of the polymer. In the polymerization of a mixture of two monomers, the structure of each macromolecule contains units of both monomers. Such a polymer is called copolymer and the process of its synthesis is called copolymerization. They are widely used commercially as fibers, plastics, composites and for coatings applications too [1-3]. They are heterochain macromolecules that possess carboxylate ester groups as an integral component of their polymer backbones. They differ from other ester containing polymers (such as polyacrylates and cellulose esters) in that the ester functionality is part of the backbone and not a pendant group.

Polyesters [4-6] are one of the most versatile synthetic copolymers. Polyesters are produced in high volume that exceeds 30 billion pounds a year worldwide [6].

A large number of polyester structures have found use in industry today which displays a wide variety of properties and applications. More detailed discussion can be found in a number of excellent books and reviews [1-3 & 6].

Carothers worked with aliphatic straight chain polyesters, which were soluble in organic liquids, low melting and had poor resistance to hydrolysis. These polyesters were not used as textile fibers[2]. The extension of these concepts later led to the discovery of nylon-6,6 in 1935 and Whinfield and Dickson developed poly(ethylene terephthalate) (PET) in 1941 [7].

A partially aromatic organic structure was necessary to increase melting temperature (Tm) above 250°C.

Now a day’s large numbers of polyesters are commercially available. These polyesters are mainly classified into four major categories, viz:
1 Vinyl Ester Resin
2 Alkyd Resin
3 Saturated Polyester Resin
4 Unsaturated Polyester Resin

1.1.1 Vinyl Ester Resin [1]

Vinyl ester resins were developed in the late 1950’s and early 1960’s i.e. just after II\textsuperscript{nd} world war. The resins were prepared by reacting glycidyl acrylate and glycidyl methacrylate with bisphenol -A. These resins are very reactive and have very short life.

Vinyl ester resins are becoming increasingly important in new industrial applications such as coating, printed circuit boards, metal foil laminates, building materials, automotive parts, rigid foams and fiber reinforced composites [8-12]. A conventional vinyl ester resin can be prepared by end capping various epoxy resins with unsaturated monocarboxylic acid [13-14]. They combine the excellent mechanical, chemical and solvent resistance properties of epoxy resins with the properties found in the unsaturated polyester resins. The cured vinyl ester resin has physical properties superior to cured conventional polyester resin, particularly corrosion resistance. This arises from difference in the number and arrangement of polar groups such as ester and hydroxyl groups and carbon- to- carbon double bonds present in the polymer chains.

In vinyl ester resins, the ester groups and carbon to carbon double bond linkages are located at the end of polymer chains, a form referred to as “structoterminal” [15] and they are distributed uniformly in the network after the polymer has been cured. A general structure of vinyl ester obtained by reacting epoxy resin with acrylic acid is as shown below.
1.1.2 Alkyd Resin [16]

Alkyds are the reaction products of polyhydric alcohols with fatty acids followed by reaction with dibasic acids. They are largely used in paint and printing ink industries [17-21].

1.1.3 Saturated Polyester Resin [16]

These are the reaction products of dibasic acids or dibasic acid chlorides with diols and largely used in textile industries e.g. Polyethylene terephthalate.
1.1.4 Unsaturated Polyester Resins

Since 1930, unsaturated polyester resins have been used remarkably for wide range of applications making them a thermosetting system of major importance [22-23]. These resins are compounded with varied fillers, reinforcements and cured by using free radical initiators to yield thermoset articles having a wide range of chemical and mechanical properties depending upon the choice of diacids, diols, cross-linking agents, initiators and other additives [24]. This versatility in the properties of the final thermoset product associated with comparatively low cost has renewed the interest in these resins as an important matrix material for wide range of applications.

Unsaturated polyester resins are the condensation products of unsaturated acids or anhydrides and diols with/without diacids. The unsaturation present in this type of polyesters provides a site for subsequent cross linking [25-26].

Ford Motor Co. Ltd. [27] synthesized unsaturated polyester resins by reacting maleic anhydride and phthalic anhydride with propylene glycol at 100°C and then at 250°C till the acid number diminished to the valueless than 50 (mg of KOH per gm of sample). Corrado and his assistants [28] synthesized low viscosity unsaturated polyester resins by
reacting maleic anhydride, phthalic anhydride and dipropylene glycol at 200°C. Ochsenbein and Olliver [30] synthesized storage stable unsaturated polyester resin by reacting maleic anhydride, propylene glycol and dipropylene glycol at 185°C under inert atmosphere.

Dabholkar and his co-workers [30] prepared polyester having acid number 45 (mg of KOH per gm of sample) from maleic anhydride, phthalic anhydride, propylene glycol and triphenyl phosphate by heating at 160°C for five hours.

In 1929, Arvin and Carothers [31] developed unsaturated polyester resins from maleic acid and ethylene glycol reacted at temperature 175°C-185°C. Afterwards, the polyesterifications of systems involving various dicarboxylic acids and dihydric alcohols have been studied by several scientists [32].

Resin having bright colour was synthesized by Freitag and his assistants [33] using dicyclopentadiene, hydrophosphorous acid, maleic anhydride and diethylene glycol. Korbar and his assistants [34] studied two-step synthesis of unsaturated polyesters of maleic anhydride, phthalic anhydride and propylene glycol. The review on the development trends in the product ion of unsaturated polyester resins was done by Penezek [35].

General purpose unsaturated polyester resins were prepared by using maleic anhydride, phthalic anhydride and propylene glycol with the molar ratio of phthalic anhydride: maleic anhydride ranging from 1:2 to 2:1 [36-37]. For thermoset products, the resultant resin was blended with styrene for cross-linking and small amount of peroxide as initiator. These types of resins are useful in making trays, shower stalls, boats, swimming pool, water tanks etc.

Acrylic modified unsaturated polyester resin having good cracking resistance, flexibility and thixotropic property were synthesized using 65 parts 0.15:1.0:0.3:0.7 molar ratio of
dicyclopentadiene: fumaric acid:ethylene glycol :diethylene glycol copolymer and 35 parts of 2-hydroxy ethylmethacrylate [38].

Denatured unsaturated polyester resin which has an excellent adhesive property to a thermoplastic resin and stability for good size was prepared by K. H. Jin et. al. [39].

Heat resistance unsaturated polyester resins modified by dicyclopentadiene were prepared by using hydrolysis addition method [40]. Simultaneous strengthening and toughening of unsaturated polyester resin by nano size TiO$_2$ powder was done by Y. Xu et. al. [41].

Chemical resistant thermostetting unsaturated polyester resins for laminates having low content of volatile organic components were prepared from isophthalic acid, maleic anhydride and propylene glycol with 35% styrene as reactive diluent [42].

Unsaturated polyester resins based on polyethylene terephthalate (PET) waste products from glycolysis by ethylene, propylene and diethylene glycols and their mixtures were prepared by V. Armanda et. al. [43].

Unsaturated polyester resins for engine peripheral parts having good sound insulation property were prepared from poly (ethylene terephthalate) based polymer 60-92%, talc 5-15%, and olefin based polymers 3-25% shows the maximum distortion in bending fracture test (ASTM D 790) [44].

Flexible polyester resins were prepared using a straight chain aliphatic dibasic acid (e.g. adipic acid or sebacic acid) or tall oil, fatty acids, maleic acid/anhydride and propylene glycol. These resins are much safer and more flexible than general purpose polyester resin. Flexibility was obtained by using diethylene or dipropylene glycol instead of propylene glycol. These are generally used in casting, picture frames, decorative furniture etc [45].
Chemical resistance resins were prepared by using higher glycols such as bis-glycol [46].

These resins contain less number of ester linkages than that of general purpose type. Therefore, they have improved resistance to alkali than that of general-purpose resins. Such resins are used in chemical processing equipment like fume hoods, reaction vessels, tanks, pipes etc [47-48].

Resilient grade resins were synthesized by two-step reaction [49-50]. First isophthalic acid was reacted with glycol to obtain polyester resins of low acid number then maleic anhydride has been reacted with the resultant product to give unsaturated polyester resin of this class, which had reactive unsaturation at the ends or between the blocks of glycol-isophthalic polymer rather than their random distribution along the polymer chain. Such type of polyester resins have greater toughness than general purpose unsaturated polyester resin. They are useful in making safety helmet gaurds, bowling balls, gel coats, air craft, automotive parts etc.

Unsaturated terephthalate based polyester resins based on 2-methyl -1,3-propanediol, a saturated dicarboxylic acid and derivatives there of, and an unsaturated dicarboxylic acid and derivatives there of are manufactured without use of a catalyst in reasonable cycle times, exhibits exceptional solubility in styrene and are thus useful in polyester molding resins[51].

The reaction characteristics of dicyclopentadiene, synthetic method of unsaturated polyester resin, mechanical performance and the application were studied [52].

There search development on unsaturated polyester resins during the year 2000-2001 was reviewed with references [53]. Unsaturated polyester resin have been made by, reaction of 2-methyl -1, 3-propanediol with ortho-, iso -, and terephthalic acid with improved strength, elongation and better corrosion resistance than the resins made from
propylene glycol [54].

A review on recent research progress in modification methods of unsaturated polyester resin, with an emphasis on the toughening and reinforcement, flame proofing, improving heat resistance and resistance to environmental medium, reducing contraction percentage of cured unsaturated polyester resin and air drying properties was done by Q. Jun-min et. al. [55].

Dainippon Ink and Chemicals, Inc., Japan prepared radically polymerizable unsaturated polyester resin with storage stability for pultrusion[56]. Unsaturated polyester resin based on dimethyl terephthalate process residue was prepared by G.Barbara et. al. [57].

Unsaturated polyester resin obtained from dicyclopentadiene and maleic anhydride showing good weather resistance and storage stability [58]. Unsaturated polyester resin prepared from isophthalic acid, maleic anhydride and neopentyl glycol was mixed with dicyclopentadiene resin and styrene to give dielectric compound for electric machines [59]. Unsaturated polyester resin having good abrasion resistance and water resistance for paint was prepared by M. Hitoshi and his assistants [60].

Sartomer Technology Company, Inc., USA prepared unsaturated polyester resin compositions comprising metallic monomers and reducing the volatile emissions of these compositions [61]. Unsaturated polyester resin synthesized in different ratios of maleic anhydride to o-phthalic anhydride and 1, 2- propylene glycol are used for preparation of carbon fiber composites to improve interfacial strength[62].

The performance of unsaturated polyester resin was evaluated under various humidity, hydrothermal and weathering conditions by V. K. Mathur [63].

Unsaturated polyester resins with good processibility, dielectric property and weather resistance were prepared with
addition of hydrotalcite with average diameter <3 µm [64]. Unsaturated polyester resin for multi-constituent stone putty with good stability and machine processibility were prepared by Schlingelhoff, Peter et al. [65]. Unsaturated polyester is compounded with paper mill muddy waste to give a molding compound [66]. Unsaturated polyester resin with good physiomechanical properties were prepared from a premix based on polyester 300, glass fiber 128, tert-butyl perbenzoate 3, Zn state 14, and Kaolin 150 parts [67].

A novel analog of nucleic acids bearing an optically active serine ester backbone, serine based nucleobase linked polyester was synthesized by A.Murata et al. [68].

Photo-sensitive unsaturated polyester resin was prepared with modification by polyepoxy by great improvement in resistance ability, thermal stability and surface hardness [69]. Fujita, Yukiko et al. prepared ship hulls comprising unsaturated polyester resin with improved weather resistance [70]. Unsaturated polyester resin with improved gloss retention and yellowing resistance was prepared by Fujita, Yukiko et al. [71]. Unsaturated polyester resin compositions comprises unsaturated polyester resin and a monomer and provides a cured product which has a >60% gloss retention after subjecting a 2000 hrs weather resistance test according to ISO standard [72].

The effect of styrene content on non-exponential and non-Arrhenius behaviour of the α-relaxation of cured unsaturated polyester resin was investigated by dynamic mechanical analysis [73].

The addition of a small amount of nanoclay (1–3 wt %) can provide excellent volume shrinkage control of unsaturated polyester (UP)/styrene (St)/poly (vinyl acetate) (PVAc) systems cured at room temperature [74]. Poly (ε-caprolactone) perfluoropolyether –poly(ε-caprolactone) block copolymers synthesized from Fomblin Z-DOL TX have been mixed with
conventional unsaturated polyester resins to prepare fluorine modified UPR. A preliminary investigation on the compatibility of uncured FUPR systems has shown that the presence of PCL blocks leads to an enhancement of compatibility with respect to pure perfluoropolyether macromers [75].

The use of di-isocyanates such as diphenylmethane-4, 4’-di-isocyanate, isophorone di-isocyanate and 1, 6-hexamethylene-di-isocyanate, with different molecular rigidity as modifiers of the thermal expansion behaviour of cured unsaturated polyester was investigated.

1.2 CLASSIFICATION OF UNSATURATED POLYESTER RESIN

On the basis of their properties unsaturated polyester resin can be classified as

1. Flexible Polyester Resin
2. Chemical Resistant Polyester Resin
3. Specialty Polyester Resin
4. General Purpose Polyester Resin
5. Resilient Polyester Resin
6. Electrical Resistant Polyester Resin
7. Fire Resistant Polyester Resin

1.2.1 Flexible Polyester Resin [16]

These can be prepared by using a straight chain dibasic acid (e.g. adipic acid or sebacic acid) or tall oil, fatty acids, maleic acid/ anhydride and propylene glycol [76]. The resulting unsaturated polyester resins are much safer and more flexible than general purpose resin. Flexibility polyester resin can also be obtained by using diethylene or dipropylene glycol instead of propylene glycol.
They are generally used in decorative furniture, castings and picture frames.

### 1.2.2 Chemical Resistant Polyester Resin [77]

The major drawback of polyester resins is their poor resistance to alkali hydrolysis. Polyester resin with improved resistance to alkali can be prepared by using higher glycols which in turn reduces the concentration of ester linkages [78].

Thus a resin containing bisglycol (the reaction product of bisphenol-A with propylene oxide) will contain less number of ester linkages than resins of general purpose type. Such resins are used in chemical processing equipments like fume hoods, reaction vessels, storage tank and rigid pipes.

### 1.2.3 Speciality Polyester Resin [77]

Resins for special application can be obtained by using different reactive monomers during crosslinking e.g. resins
with improved heat resistance can be prepared by using triallyl cyanurate (I) in place of styrene [79].

\[ H_2C=CH-CH_2-O-C-N \]
\[ \quad C-O-CH_2-CH=CH_2 \]
\[ \quad 0-CH_2-CH=CH_2 \]

(I)

### 1.2.4 General Purpose Polyester Resin [16]

Such polyester resins are prepared by the reaction of a phthalic anhydride (PA), maleic anhydride (MA), and propylene glycol (PG) [80] with the molar ratio of phthalic anhydride: maleic anhydride ranging from 2:1 to 1:2.

The resultant polyester resin is then blended with styrene in the ratio 2:1 for cross linking in the presence of peroxide initiators. These types of resins are useful in making trays, boats, shower stalls, swimming pools and water tanks.
Where the value of x and y is dependent on the ratio of phthalic anhydride: maleic anhydride used in the synthesis.

1.2.5 Resilient Polyester Resin [77]
Polyester resins of this type fall between the rigid general purpose type and flexible types [81-82]. Such resins can be obtained by first reacting isophthalic acid and glycol to give a polyester resin of low acid number. Maleic anhydride is then added and the esterification is continued. This gives polyester chains having the reactive unsaturation at the ends or between the blocks of glycol - isophthalic polymer rather than their random distribution along the polymer chain. Such resin has a greater toughness as compared to general purpose unsaturated polyester resin.

1.2.6 Electrical Resistant Polyester Resins [77]
Electrical resistant polyester resins can be prepared by using dibasic acids e.g. isophthalic acid, maleic anhydride and neopentyl glycol [83] or tetrabromo bisphenol –A [84] in place of phthalic anhydride or propylene glycol.

Electrical resistance of polyester resins can be further improved by blending with various additives such as antimony trioxide [85], kaolin [86], mica [87] and calcium carbonate [88]. Such types of resins are generally used in printed circuit board, electrical appliances and electronic equipments.

1.2.7 Fire Resistant Polyester Resin [77]
Fire resistant polyester resins can be prepared by using halogenated dibasic acids e.g. tetrachlorophthalic anhydride (I), tetrabromophthalic anhydride (II) [89], dibromoneopentyl glycol (III) [90] or tetrabromo bisphenol -A (IV) [84] in place of phthalic anhydride or propylene glycol.

Fire resistancy of polyester resins can be further improved by blending with flame retardant additives such as triphenyl phosphate and antimony trioxide [91]. Such types of
resins are generally used in fume hoods, electrical equipments, building panels and navy boats.

1.3 GENERAL SYNTHESIS OF POLYESTER RESINS

Polyester resins have traditionally been categorized as step or condensation polymers (along with polyamides, polyureas and others) because of the loss of water or other small molecule with each step of chain growth to distinguish them from addition polymers. However, polyesterification, involves several steps, which markedly distinguishes them from both classes of polymers. The products of polyester synthesis from difunctional monomers are linear species as well as cyclics.

A number of synthetic approaches exist for the preparation of polyesters [1, 3 & 92]. These include direct esterification, transesterification (ester interchange) and the reaction of alcohols with diacid chlorides. The general reaction of each of the three methods is illustrated in Scheme 1.1. Each method involves nucleophilic addition to the carbonyl group, which is facilitated by the polar nature of the carbon-oxygen bond and the ability of the carbonyl oxygen to assume a formal negative charge. Each step of the nucleophilic addition is reversible, except in the case of the reaction
involving the diacid chloride. Here, the by-product (HCl) is less nucleophilic than the alcohol and is typically removed as the reaction proceeds.

Direct esterification and trans esterification are slow equilibrium processes. Catalysts are generally required to increase the rate of reaction. Both acidic and basic catalysts can be used. Acidic catalysts include protonic acids, Lewis acids and titanium alkoxides. These acidic catalysts coordinate with the carbonyl oxygen, rendering the carbonyl carbon more susceptible to nucleophilic attack. A general reaction mechanism is shown in scheme 1.1:

\[
\begin{align*}
\text{Direct Esterification} & \\
\text{Transesterification} & \\
\text{Reaction of Alcohols with Acid Chlorides} & \\
\end{align*}
\]

**Scheme -1.1 General mechanism for the synthesis of polyesters**

Weak basic catalysts convert the reacting hydroxyl group to the corresponding (and more nucleophilic) alkoxide anion, which is then more effective intermediate for the inter change process. The three types of polyester synthesis are discussed
in detail below, along with the much less common addition polymerization of cyclic esters. The synthetic approaches exist for preparations of polyester resin are as follows:

1 Direct Esterification
2 Transesterification
3 Acylation

1.3.1 Direct Esterification

Direct esterification is the reaction of a diol with a dicarboxylic acid (or cyclic anhydride) or the self-condensation of a hydroxycarboxylic acid as shown in Scheme 1.2. The by-product of direct esterification is water. Direct esterification is a slow process. The carboxylic acid functional group provides protons to catalyze the reaction, but since the concentration of carboxylic acid groups decreases as conversion increases, it is often necessary to employ an additional catalyst. These catalysts include protonic acids or Lewis acids, titanium alkoxides, and dialkyl-tin(IV) oxides. Because this is an equilibrium process, water must be effectively removed in order to push the equilibrium toward high molecular weight polymer. To achieve this, high temperatures are required. Therefore, a reaction temperature must be chosen which strikes a balance between what is required for the reaction to proceed as a homogeneous melt, and that, which minimizes the risk of thermal degradation over the required reaction time. The side reactions, which can occur, include readily decarboxylated acids or isomerizable cis-substituted reactants, which may be transformed either partly or wholly to trans.

Achieving stoichiometric equivalence for the A-A/ B-B systems is difficult since the diol is usually quite volatile. Therefore, the diol is charged in excess with respect to the diester in the initial stage. The common reaction mechanism is shown in scheme 1.2:
Transesterification (also known as ester exchange or ester interchange) involves a two-stage reaction of a dialkyl (i.e. dimethyl) ester (instead of a dicarboxylic acid) with a diol in an ester interchange process and is generally carried out in the presence of a proton donating or weak basic catalyst. Such catalysts include the carbonates, alkanoates, hydrides or alkoxides of sodium, lithium, zinc, calcium, magnesium, and bimetallic alkoxides such as NaHTi(OC\(_4\)H\(_9\))\(_6\), MgTi(OC\(_4\)H\(_9\))\(_6\), and CaTi(OC\(_4\)H\(_9\))\(_6\). The by-product is an alcohol (i.e. methanol). This procedure is widely applicable for the formation of homo and copolyesters of aliphatic or alicyclic diols with aliphatic, alicyclic, aromatic or heterocyclic dicarboxylic acids.

At the end of the first stage of the reaction, the major product is a bis (hydroxyalkyl) ester and/or an oligomer thereof. In the second stage, the ester is subjected to polycondensation.
condensation by alcoholysis, forming the high molecular weight polyester. In this stage the by-product is the diol for each step of chain growth. The general reaction is illustrated in Scheme 1.3.

**Scheme-1.3 General reaction mechanism of transesterification**

The first stage is usually carried out at 150° -200°C until the evolution of the alcohol is complete. The second stage is usually carried out at 220° -290°C under reduced pressure in order to facilitate complete removal of the diol. The choice of the temperature of the second stage of melt polymerization is governed by the requirement that the polymer remains as homogeneous melt. It must, therefore, be at least 20°C above the highest melting temperature of the
final product. Since each stage is an equilibrium process and therefore reversible, the equilibrium can be forced to favour polymerization by continuous removal of the alcohol and diol by-products.

As in direct esterification, 1:1 stoichiometry is extremely difficult to insure due to the volatility of the diol as well as the tendency of many of the diesters to sublime. The diol is charged in a 50 percent excess (by moles) with respect to the diester. This helps insure 1:1 stoichiometry in the end, but it also serves to drive the first stage of the reaction to completion at a faster rate.

Another procedure, which avoids the high temperatures and long melt reaction times, involves interrupting the polymerization at an intermediate stage and allowing the product to solidify. The material is then pulverized and heated either under vacuum or in a stream of inert gas at a temperature, which is above the Tg but about 10⁰ -20⁰C below the Tm where the chains have some mobility and the catalyst is active, but where the polymer is thermally stable. This method of solid state polymerization often results in molecular weights much higher than those achieved by melt processes [6].

1.3.3 Acylation

A third approach for the synthesis of polyesters is the reaction of diacyl chloride with dihydroxy compound to generate a polymer. This reaction can be performed in the melt as well as in a high boiling, inert solvent. HCl is the by-product of such reaction [93-95]. Typically, the reaction proceeds rapidly and no catalyst is required. Another method, however, is the Schotten- Baumann reaction in which a base such as pyridine is used to catalyze the reaction and act as an acid acceptor of the HCl produced [96-98]. This reaction can then be performed at ambient temperatures.
The alternative route to acylation is an interfacial polycondensation reaction. Here two solutions are first formed: one consisting of the diacid chloride in an organic solvent and the other consisting of the diol (such as a bisphenol) in an aqueous alkali solution. The two solutions are rapidly agitated. The polymer forms immediately at the interface and either precipitate or remain soluble in the organic phase. A Phase Transfer Catalyst (PTC) such as tetraalkylammonium halide is usually added. Interfacial polymerizations do not precisely require 1:1 stoichiometry in the bulk because 1:1 stoichiometry favoured at the interface. These types of reactions are diffusion controlled. The solution or melt polycondensation methods, however, require high purity starting materials.

1.4 PROPERTIES AND APPLICATIONS OF AROMATIC POLYESTERS

Aromatic polyesters (or polyarylesters) have a wide variety of commercial uses. Much of the early work was directed towards textile fiber applications after the introduction of poly (ethylene terephthalate). Within the series of increasing methylene groups, poly (ethylene terephthalate) (PET) and poly (butylene terephthalate) (PBT) have been studied the most extensively. The first three members of the poly (methylene terephthalate) series (alkane group = ethane, propane, butane) have remarkably different properties than the remaining members in the series. They melt above 220°C. The higher members of the series have melting temperatures below 160°C [99].

The two most important types of polyesters are based on PET and PBT, which between them have over 95% of the thermoplastic market for thermal injection moldable parts. When textiles are considered, only polyesters based on ethylene glycol, 1, 3-propanediol and 1, 4-butanediol are
suitable due to their higher melting temperatures and solubility. For more detailed information, many excellent books and reviews have been written unsaturated polyesters [100-104].

1.4.1 Poly (ethylene terephthalate)

PET is a step or condensation based homopolyester based on terephthalic acid or dimethyl terphthalate and ethylene glycol and has the repeat unit:

![PET Repeat Unit](image)

Unmodified PET plastics have been known for many years, but many molded parts were unsatisfactory due to an extremely low rate of crystallization [104].

The melting point of commercial PET usually falls in the range of 255°C-265°C. Because of this slow crystallization rate, PET is best suited for applications where crystallinity can be enhanced by mechanical orientation like soft-drink bottles, biaxially oriented blown films, fibers etc. The glass transition temperature of PET varies depending on the polymer purity, degree of crystallinity and method of determination [104].

PET with a weight average molecular weight (Mw) of 35000-40000 g/mole is suitable for oriented films and textile fibers; however Mw of about 80,000 g/mole is necessary for the higher impact strength needed for injection molded parts [105].

PET and PBT have good resistance to water, weak acids and bases, ketones, alcohols, glycols, ethers, aliphatic hydrocarbons and chlorinated hydrocarbons at room
temperature. Strong bases rapidly degrade these materials at any temperature or aqueous bases above 50°C. This instability is exploited in their cycling of PET soft drink bottles by degrading them back to starting materials [106].

PET is synthesized via melt polymerization. Unlike many other poly(alkylene terephthalates), synthesis of PET requires two component catalyst system in order to generate high molecular weight material [107]. One example of such a catalyst system utilizes zinc acetate and antimony trioxide. These two catalyst systems are in contrast to the single catalyst systems which previously used lead acetate [1,6 & 104].

At high temperatures and long time periods, such as those used in the synthesis of PET, thermal degradation can occur. Although many reaction schemes have been proposed, there has been little hard evidence that exists to favour one over another. It is generally accepted that PET degrades with random chain scission at the ester linkages. The methylene group is believed to be the principle point of chain weakness. The degradation of PET involves β-scission which leads to carboxyl and vinyl ester groups which can then react via an acetal ester intermediate forming arboxylic anhydride linkages plus acetaldehyde. Further reactions include polymerization of some vinyl ester groups to species which themselves suffer thermal scission and condensation of some acetaldehyde to polyene [6 &108].

Moisture causes rapid hydrolytic degradation at melting temperatures and can also be enhanced at lower temperatures in an oxidizing atmosphere. The mechanism of PET thermal degradation has been the subject of several studies [109-113].
1.4.2 Poly (butylene terephthalate)

PBT is a step growth or condensation homopolymer based on 1, 4-butanediol and dimethylterephthalate and has the repeat unit:

\[
\begin{align*}
&\begin{array}{c}
\text{PBT} \\
\end{array}
\end{align*}
\]

PBT is one of the faster crystallizing polymers and unlike PET, does not require nucleating agents or orientation to induce crystallization. Its melting point is $230^\circ$C, depending on sample preparation and annealing time. PBT resins contain fewer impurities than PET since the side reactions of the polymerization (tetrahydrofuran and butadiene) are volatile. Its glass transition temperature varies widely with crystallinity and the choice of measurement method. $T_g$ range from $30^\circ$C to $50^\circ$C, but have been reported as low as $20^\circ$C [114].

Due to its high crystallization rate, PBT is often used in injection molding applications, where the high rates of crystallization allows short processing cycles.

PBT exhibits good electrical insulation properties which are virtually independent of temperature and humidity [104]. In general these materials do not exhibit good weather resistance without the aid of stabilizers. Polymer degradation is the result of UV exposure, especially in the presence of heat, moisture, oxygen or atmospheric pollutants. The degradation is manifested as a loss in impact strength [115]. PBT like PET, is synthesized via melt polymerization methods and is also susceptible to $\beta$-scission after long reaction times at high temperatures. In this case, the degradation products are tetrahydrofuran and a carboxyl end group, which leads to carboxyl functionalities and 1, 3- butadiene.
PBT has a large number of applications which includes electronics, automotive, house wares, lighting, power tools, sporting goods and plumbing. Specific applications include computer housings and automobile bumpers.

1.5 PROPERTIES AND APPLICATIONS OF ALIPHATIC AND CYCLOALIPHATIC POLYESTERS

The properties of polyesters in general, as in many polymers are determined by the geometry, symmetry, polarity and segmental mobility of the chain structures. Their intermolecular reactions are relatively weak and their properties are therefore more sensitive to molecular geometry than more polar materials such as polyamides and hence, have a wider use range [6].

Aliphatic and cycloaliphatic polyesters are substantially resistant to oxidation by air or ozone under normal conditions, but are degraded rapidly by ammonia, hydrazine, warm alkali solutions and primary or secondary amines, which cleave the ester linkage forming hydroxyl groups and the salt or amide derivatives of the carboxyl functionality. Cycloaliphatic based polyesters contain two tertiary protons per repeat unit, which adds to the molecule's thermal instability. These materials are light stable and hydrophobic in nature and this provides extra resistance to chemical attack by aqueous based reagents. Hydrolysis can occur at elevated temperatures or by steam [6 & 116].

The melting points of linear aliphatic polyesters increase with increased methylene/carboxylate ester group ratio in the repeat unit. In addition, polyesters with an even number of methylene groups are consistently higher melting than those containing an odd number of methylene groups [92]. These materials are capable of forming fibers at degrees of polymerization (Dp) of about 40. Aliphatic polyesters do not
absorb in the visible or normal range UV spectral regions, but they do absorb in the infrared.

The properties of ring containing polyesters are dependent on the conformation, symmetry and structure of the cyclic unit. Typically, a ring containing polyester composed of predominately cyclic component (whether it be aromatic, alicyclic or heterocyclic), then the polyester, if it contains semi - crystalline regions, will have a melting temperature considerably higher than those of the acyclic polyesters. This trend is also reflected in the glass transition temperature, which is also higher for both amorphous and semi – crystalline materials. This is a result of the higher restriction of chain motion in the ring as compared to the acyclic counterparts [6].

With the introduction of a cycloaliphatic moiety into the unit, the ratio of cis to trans isomers becomes an important factor and can greatly affect the ultimate polymer properties. Polyesters with high trans content are usually semi - crystalline, while those with high cis content are amorphous, or have a much lower Tm. For example, poly (1,4-cyclohexanedicarboxylate) containing the all trans isomer has a melting temperature of 50°C, while the all cis derivative is amorphous. Poly (1,4-cyclohexanedicarboxylate) synthesized from the all trans isomer has a melting temperature of 124°C while the cis derivative has a Tm of 55°C [6].

Aliphatic or cycloaliphatic polyesters are used in applications, which require UV resistance since the aromatic polyesters absorb strongly in the UV region resulting in chain scission and subsequent degradation. Because of their combination of low melting points, solubility and limited hydrolytic stability, most acyclic polyesters are not used as structural materials. Their low glass transition temperatures
enable them to be used as plasticizers and components in polyurethanes.

Some alicyclic containing polyesters are used commercially as fibers. For example poly (cyclohexane-1, 4-dimethylterephthalate) containing about 70% of the alicyclic rings in the trans configuration was commercially introduced in 1955 as Kodel® by the Eastman Kodak Company [1]. In fact, most aliphatic polyesters are utilized as one part of a copolyester block copolymer or blend. More extensive discussions of the properties and applications of linear acyclic polyesters are found in various books and reviews [1-3, 6].

1.6 INHIBITORS

The styrene containing unsaturated polyesters will polymerize at room temperature without the use of a catalyst if given enough time. Such premature reaction can be effectively prevented by use of inhibitors.

Typical effective inhibitors that are in commercial use are hydroquinone, p-butylcatecol, aromatic amines, picric acid and quinines [117]. There are hundreds of other compounds that are effective as inhibitors but their effect on both cure characteristics and properties of the cured products has not been sufficiently established. Oxygen is a powerful inhibitor for the polymerization of unsaturated polyesters, reacting rapidly with the radicals formed in the resin, thus rendering them useless for subsequent reaction.

1.7 CHARACTERIZATION OF POLYESTER RESIN

As mention above various grades of unsaturated polyesters can be synthesized. However to meet the end use applications some processing is to be carried out. In order to make the processing easy it is essential to have the knowledge about the specifications like end groups, degree of polymerization, spectral characteristics etc.

In the specifications, the acid number is of prime
importance. The acid number or acid value of the polyester resin can be determined by simple acid base titration using alcoholic alkali [118]. The common aliphatic acid and phthalic acid content may be determined quantitatively by the procedure of Swann [119]. Phthalic acid may be determined by ultraviolet absorption by the method of Shreeve and Hether [120] or polargraphically by the method of Whitnach and Grantz[121]. Hobart [122] has determined maleic and fumaric unsaturation directly on the polyester by polarographic methods. Unsaturation in the polyester resin can be determined by iodine values using Wijs solution [123]. The ester group formed during polycondensation can be estimated by alcoholic saponification for which the most widely used method is decomposition of ester linkage using method advocated by Kappelmeler [124].

R. K. Nair et. al. [125] carried out the kinetic study of unsaturated polyester resin by determining acid values and viscosity at different temperature and time interval. Benami et. al. [126] developed an equation to determine the intrinsic viscosity by single concentration of polymer solution.

Several authors [127-129] have characterized polyester by infrared spectroscopy. The molecular weight of low molecular weight oligomers can be determined by vapour pressure osmometry and gel permeation chromatography [130]. J. H. Done et. al. [131] have studied the application of high performance liquid chromatography for characterization of polymers.

1.8 CURING

Curing or cross - linking is a process by which the material from soluble and fusible state transforms into insoluble and infusible cross- linked state.

The expansion of unsaturated polyesters into varied fields of application has brought a demand for special resins
requiring peculiar curing conditions. Although in many cases fast curing at high temperature can be tolerated and may even be desirable, there is an increasing number of applications that require low exothermic temperature. At the same time fabrication of pieces requiring such low curing temperatures must be economical, i.e. the cure must be attained within a minimum time. The properties of the cured polyester are largely imparted by the raw materials added to the polymerization reaction, the reaction conditions, the type and concentration of the copolymerizable monomer, and the curing conditions. If products of high quality are required it is usually necessary to ensure a fairly high degree of cross-linking i.e. a relatively high percentage of unsaturation in the polymeric chain is needed. This however, results in resins that produce high exotherm temperature during the cure. Although the major contributions to the exotherm results from the amounts of unsaturated acid added to the reaction, the amount and type of monomer as well as the type and properties of saturated acids and glycols employed, also affects the exotherm behaviour of polyesters[132]. A number of photochemical methods have been developed to cure unsaturated polyester coatings or transparent articles [133-135].

1.8.1 Catalyst For Curing

The cross-linking of unsaturated polyesters is a free radical polymerization initiated with compounds often referred to as “Catalysts”, although they are in fact consumed during the reaction. The most widely used initiators are peroxides, diacylperoxides, peresters, perketals, ketones, dialkyl peroxides and hydroperoxides [136]. Some peroxide free initiators have also been reported [137-138].

The decomposition of initiators is inducted by heat in the case of molding compounds or by accelerators at temperatures below the decomposition temperature of the
initiators in the case of cast polyester resins. Two types of accelerators are used; metal salts mainly cobalt salts and amines.

The oxi-reduction of metal salts by peroxides produces free radicals. The process is very efficient since both lower and higher valences of cations participate in there action (Scheme-1.4). Peroxides decomposition is promoted by tertiary amines following, the scheme-1.5, where free radicals are formed from both benzoyl and amino moieties [139].

\[
\begin{align*}
ROOH + Co^{+2} & \rightarrow Co^{+3} + RO^{-} + OH^- \\
ROOH + Co^{+3} & \rightarrow Co^{+2} + ROO^{-} + H^+ \\
RO^{-} + Co^{+2} & \rightarrow RO^{-} + Co^{+3}
\end{align*}
\]

**Scheme -1.4 Oxi-reduction of metal salts by peroxides**

**Scheme -1.5 Peroxide decomposition by tertiary amines**
Metal-ion complexes with amines have been claimed to improve the gel time [140] and light resistance [142-144] and to lower the inhibition effect of oxygen in air. It has also been reported that thiol salt mixtures have good performance for unsaturated cross linking [145].

Accelerators included in polyester chains are significantly better than those simply mixed with the resins. This is the case where the polyester is synthesized in the presence of small amounts of metal, maleates or aminoethanols [146-148] or after chemical modification of polyester chains with primary or secondary amines [149].

Unsaturated polyesters may also be cured by microwaves [150], high frequency electric fields [151] or by UV or visible irradiation using photo initiators [142-143].

Organophosphorus compounds used as photo initiators for unsaturated polyester resins [152]. The studies of effect of resin chemistry on curing of unsaturated polyester resin were carried out by Y. Huan and L. L. James [153].

The curing behaviour of unsaturated polyester resin in the presence of different initiators was studied by means of differential scanning calorimetry (DSC) [154]. An interest has been developed in the use of vanadium naphthenates as accelerators. In 1956 the author [155] found that if MEKP was added to a polyester resin containing vanadium naphthenate the resin set almost immediately.

The efficiency of H$_2$O$_2$, methyl ethyl ketone (MEK) peroxide, ter-butyl peroxide and cumene peroxide along with ascorbic acid based redox system of sulfonato unsaturated polyester resin micro-emulsions were studied [156].

1.8.2 Crosslinking Agents

The vinyl monomers used to effect crosslinking include styrene or a combination of styrene with other copolymerizable monomers such as $\alpha$-methyl styrene, methyl
methacrylate, diallyl phthalate, triallyl cyanurate etc. Although a large number of monomers like vinyl toluene, divinyl benzene, vinyl acetate, vinyl 2-chloroethyl ether, N-vinyl pyrrolidone, 2-vinylpyridine etc. can be copolymerized with unsaturated polyester in conjunction with or in absence of styrene [144].

1.8.3 Crosslinking Mechanism

After addition of the vinyl monomer, crosslinking begins on introduction of an initiator, usually organic peroxide. Crosslinking occurs via free radical polymerization. In the common styrenated polyester three types of radicals are formed, those of fumarate, styrene and the catalyst. In order to obtain a high quality product, it is desirable that the styrene and fumarate radicals react either alternatively or in the proportion existing before crosslinking occurs [157].

![Crosslinking mechanisms](image)

**Scheme -1.6 Crosslinking mechanisms**

The initial formation of free radicals occurs through the catalyst, which is added in concentrations of 0.5- 2.0%
depending on the type of catalyst and the temperature of the medium. There activity ratios of the two unsaturated species are not affected by the length of glycol in the polyester chain. The mobility of the unsaturated units that have not yet reacted is reduced not only by the increasing viscosity of the resin but also by the incorporation of these units into the three dimensional network, thus, the diffusion of unsaturated acid units towards the growing radical chains is initiated to a greater extent than the diffusion of the remaining free styrene molecules towards the radical chains. Reaction of the fumarate units is therefore expected to drop rapidly when the conversion has reached a certain degree, after which curing proceeds primarily through the reaction of styrene units. It has been shown that styrene does not homopolymerize under the reaction conditions and no measurable amount of styrene homopolymer is present in the cross linking polyester [145]. The structure of cured general-purpose polyester can be described as follows.

![Chemical structure of cured polyester](image)

Where, \( n : 1 \) to \( 10 \)

The network is composed of two polymolecular species, namely, the polycondensation chains and the copolymer chains. Both are connected with each other through covalent bonds with the fumarate groups i.e. both types of chain polymers have fumarate groups in common, thus forming a network.
The average crosslinking consists of 1.5-2.5 styrene molecules; however the actual links vary greatly in length. Also a small percentage of unsaturated groups remain unreacted, imparting some flexibility to the cured products. In general purpose polyesters, the proportion lies between 2-7% [158].

A schematic representation of the three dimensional polyester network indicates that the structural rings are composed of four segments: two segments that are part of the polyester chain and two segments that are composed of polymerized styrene. In actual polyester network itself it is more probable that these polymeric rings, of which the network is composed, contain more than four chain segments. The spatial representation of cured polyester is illustrated in figure -1.1. Since the individual chains may assume all shapes in the styrene solution, such a random copolymer has a greater statistical chance of being formed than the schematic four - sided structure. The average length of the segment depends upon both the styrene concentration and the number and type of reactive double bonds alone the polyester chains.
1.9 STRUCTURE PROPERTY RELATIONSHIPS

A unifying concept correlating the established structural features of the three dimensional polyester network with the performance properties of the cured products is not available. However, there are number of individual interrelations that permit prediction of these properties to a certain degree. The property that has been most extensively investigated in relation to the chemical structure of different polyesters is the melting point. Many of the structural groups reported to affect the melting points of linear polyesters in certain ways also affect the physical properties of cross-linked polyesters. As then molecular weight of the unsaturated polyesters increase the cured product exhibits improvement in certain of their properties, such as heat distortion temperature, hardness, tensile strength, flexural strength and chemical resistance.
until a constant value is reached. The notable effect on the melting points of linear polyesters by odd and even number of methylene groups in both acid and glycol components is also parallel by effects on the values of other physical properties of unsaturated polyesters such as hardness, impact resistance and heat distortion temperature [157].

1.10 APPLICATIONS

Unsaturated polyesters have been used commercially in huge quantities for over two decades. Their initial use was as coating in wire insulation was followed by the rapid development of glass-reinforced resins, using hand lay-up and matched metal die molding technique. Cast products of polyesters have long been in use. Large scale application of unsaturated polyester lies in the use of compounded mixes for auto body repair, adhesions to metal, short hardening times, and adhesion to auto parts are major factors in their suitability for their use.

1.10.1 Casting

Cast polyester resins are prepared without use of any reinforcement and the mechanical properties of the heat cured final compound are only of secondary importance. Among the applications, which use no fillers, are the embedding of parts and the manufacturer of buttons and varnishes. However most applications employ large amounts of low cost fillers, polyesters, cements, simulated marbles, bolts and various encapsulation compounds [160].

1.10.2 Gel Coats

To produce molded parts affording surface with an attractive appearance, high gloss and environmental resistance, pigmented, filled and prepromoted polyester resin paints called gel-coats, are sprayed with a peroxide initiator
on to the mold before reinforcement with gloss and laminating resins [161-162]. Generally these gel coats contain thixotropic additives such as pyrogenated silica in order to avoid sagging on vertical surfaces. Gel coats are used primarily in the marine industries, as the exterior paint layer for boats.

### 1.10.3 Laminates

Laminating resins reinforced with glass fibers and are usually not cured under pressure [163-164]. Various processes for lamination are as follows;

(a). Hand Lay-up Molding
(b). Spray-up Molding
(c). Compression Molding, Transfer Molding and Resin Transfer Molding
(d). Injection Molding
(e). Reaction Injection Molding
(f). Pultrusion Process
(g). Filament Winding Process

#### 1.10.3(a) Hand Lay-up Molding

Hand lay-up molding is the method of laying down fabrics made of reinforcement and painting with the matrix resin layer by layer until the desired thickness is obtained. This is the most time and labour consuming composite processing method, but majority of aerospace composite products is made by this method in combination with the autoclave method. Due to the hand assembly involved in the lay-up procedure, one can align long fibers with controlled orientational quality. Another advantage of this method is the ability to accommodate irregular shaped products. Such advantages are utilized in low performance composites including fiber-glass boat and bathtub manufacturing.
1.10.3(b) Spray-up Molding

Spray-up molding is much less labour intensive than the hand lay-up method by utilizing a spray gun and a fiber cutter. However, only short fiber reinforced composites can be made. A continuous fiber is fed into the cutter and chopped. The chopped fiber is sprayed upon a mold with the stream of resin and catalyst delivered through separate nozzles. The sprayed mixture of fiber and resin soon cures on the mold at room temperature and the product is produced. Because of the spraying operation, large and complex-shaped objects can be easily made.

1.10.3(c) Compression Molding, Transfer Molding and Resin Transfer Molding

Compression molding uses a pressure to compress either dough of resin and fiber mixture or the layers placed by a hand lay-up method or mechanical means, typically at an elevated cure temperature. With the compressive force, the void content is lower than the ordinary atmospheric pressure processing method.

A matched die mold allows shaping of the composite precursor into reproducible shapes. Although a compression molding machine is used, it is still a labour intensive method as the dough or layed-up materials must be weighed and hand-fed into the mold.

Transfer molding is the improved version of compression molding from the material metering point of view as the fiber/resin mixture is transferred from the reservoir into the mold cavity by the pressure. However, a long-fiber reinforced composite cannot be made. This method is nearly identical to a plunger-type injection molding operation based on the material flow. The term "transfer molding" is used for a compression pressure operation while plunger-type injection
molding is obviously carried out in an injection molding machine.

Resin transfer molding is the same as the ordinary transfer molding except that only the resin is transfer molded into the mold cavity where fabrics are placed beforehand. Preforms of glass fibers and other reinforcements can be made with short fibers and some times continuous fibers. Preforms must be made to withstand the pressure of resin injection in order to avoid compression of the fibers during mold filling which would lead to non-homogeneous fiber distributions in the final part. Curing is carried out typically after filling at an elevated temperature.

### 1.10.3(d) Injection Molding

Injection molding is probably the most extensively used method for processing short-fiber reinforced thermoplastics. The fiber/resin mixture, whether it is preblended or fed as a physical mixture, is fed into the hopper and transfer red into the heated barrel. The material softens by the heat transfer from the barrel wall. At the same time, the screw rotates to apply highshear process to further heat the material and fill the barrel. The molten material is collected in front of the screw by the rotation of the screw, and then injected with a high pressure into the mold cavity through the runner and the gate. The mold is cooled below the solidification temperature of the resin in case of thermoplastics composites. The level of automation of this method is the highest among many processing methods. Due to the intensive mixing with high-shear and passage through a narrow gate, extensive fiber damage occurs; therefore, injection molding for composite materials is suitable only with short fiber reinforced or particulate-filled polymers.

There is a critical length of fibers below which the fiber length does not degrade. The critical length is determined by
the rheological properties of the composite mold, fiber properties and instrument factors. Less fiber damage occurs when a plunger - type injection molding machine is used rather than a screw-type injection molding machine. Because the plunger - type injection molding machine does not achieve a high degree of mixing in the machine, the raw materials must be thoroughly mixed prior to feeding.

1.10.3(e) Reaction Injection Molding

Reaction injection molding (RIM) is one of the newest processing methods. Instead of using already polymerized materials as matrices, highly reactive monomeric or oligomeric ingrediants are placed in two tanks which are then quickly mixed by impingement, and injected into the mold cavity. As soon as the two materials are mixed, chemical reaction begins to form a polymeric matrix, which completes typically within 5-30 seconds. Thus, the major portion of the RIM machine is a high pressure pump and a metering system. Again, with high intensive shear, only short fibers and fillers can be used as reinforcements. However, RIM utilizes low viscosity chemicals and this allows the pre placement of continuous fiber -woven fabrics in the mold in the same manner as resin transfer molding. Distinction is made between these two methods based on the preparation of the resin precursor. When the resin formulation is already made, the method is called resin transfer molding while if the resin is prepared insitu by an impingement or static mixer, the method is termed RIM.

1.10.3(f) Pultrusion

Pultrusion is used only for polymer composite processing. A bundle of fiber rovings is passed through a wet resin bath, squeezed into a desired shape, passed through a heated die and cured into a final composite. The solidified composite, typically reinforced unidirectionally with
continuous fibers or sometimes bidirectionally is pulled by a puller to continuously feed the uncured portion of the wet fibers into the hot die, thus the name, "pultrusion". This is one of very few continuous processing methods for continuous fiber reinforced composites. Only constant cross-sectional products can be made.

1.10.3(g) Filament Winding

Filament winding is also a unique processing method for polymer composite processing with a continuous reinforcing fiber. Resin-wet rovings are wound with a certain pattern around a mandrel. The wound mandrel is then placed into an oven and cured to a solid composite. Due to the controlled tension, squeezing action and controlled winding pattern, the fiber content can be very high to produce composites with one of the highest mechanical properties. The winding process is time consuming and is the cause of low productivity. However, due to its very high mechanical properties with automated operation, it is actively evaluated.

1.10.4 Molding

Reinforced unsaturated polyester resins may be cured at high temperature and/or pressure using matched metal dies. This is referred to as molding. The use of semi finished compounds that may be molded to sheet molding compounds "SMC" [165-166] or injected (bulk molding compounds "BMC") has become increasingly important particularly in automotive applications for weight reduction [167]. SMC and BMC contains highly reactive unsaturated polyester resins [168], fillers, high temperature initiators, mold release agents (Zinc or calcium stearate), pigments, thermoplastics to prevent shrinkage and a thickening agent. In the case of SMC, two layers of these mixtures are used to sandwich chopped glass strands or continuous roving between two polyethylene sheets.
The roll of compound is then sliced and molded under pressure and at high temperatures. In the case of BMC, all the ingredients are blended with short glass fibers in an appropriate mixture and injection molded. Mechanical properties obtained by BMC are low compared to those obtained from SMC.

In order to replace metals in automotive exterior parts by cured unsaturated polyester resins, excellent dimensional stability and accurate mold surface appearance must be achieved. Some modified polyester resins associated with reactive initiators have such properties without additives [169]. However, low profile or low shrink additives for surface finish and for dimensional stability respectively are always used to compensate for the chemical shrinkage occurring during the cross-linking monomer [165&170].

1.10.5 Fiber Reinforced Plastics
The overwhelming bulk of polyester resin produced commercially today are reinforced with glass fiber, generally glass fiber mat are molded into a variety of end products where high strength, good chemical resistance or durability, or the ability to make very large structures is important. Many books and other publications are available which describe in detail the various molding techniques used in reinforced plastics [171-173].

1.10.6 Miscellaneous Applications
Unsaturated polyesters are also used for some miscellaneous purposes e.g. in preparation of low density foam [174-175], printing ink, artificial marbles [174-175], cement coatings and printed circuit boards [178]
1.11 FIBER REINFORCED MATERIALS

There are so many fibrous reinforcement available for preparing composite materials, like jute fiber, carbon fiber, wood flour, glass fiber, cotton, paper etc. in form of discrete fibers, fibers stands or woven or nonwoven fabrics. (179-186)

1.12 JUTE FIBER REINFORCED COMPOSITES

The recent years there is an increasing interest in natural fibers as a substitute for glass fibers mainly because of their low specific gravity, low cost, as well as their renewable and biodegradable nature [187].

Among all the natural fibre reinforcing materials, jute appears to be a promising material because it is relatively inexpensive and commercially available in the required form. However, its mechanical and physical properties are highly inconsistent and depend on geographic origin, climatic growth conditions and processing techniques [188]. Jute is one of the most important natural vegetal fibres, and is produced in India, Bangladesh, Thailand, Vietnam and other countries. It contains 56–64% cellulose, 29–25% hemicelluloses, 11–14% lignin and a small proportion of fats, pectin, ash and waxes [189]. Munikenche Gowda et. al. [188] studied some mechanical properties of unsaturated jute reinforced polyester composites. Saha et al. [190] studied of jute fibre reinforced polyester composites by Dynamic Mechanical Analysis.

Lignocellulosic fibres like sisal, jute, coir, pineapple and banana have been used as reinforcements in thermoset matrices. Among these fibres, jute is of particular interest in that its composites have high impact strength in addition to having moderate tensile and flexural properties compared to other lignocellulosic fibres [191].

Several studies have been reported on jute-reinforced polymer composites, especially with epoxy, phenolic, and polyester matrices [192-195]. Roe and Ansell [192] have
studied the mechanical properties of jute reinforced polyester composites containing uniaxially oriented jute fibres. Bhattacharya et al. [193] have made composites with jute fibres in a phenolic resin. Sridhar et al. [194] have studied the tensile, flexural and impact properties of unidirectional and bidirectional jute/glass hybrid polyester composites. Varma et al. [195] have studied the mechanical properties of hybrid composites of glass and modified jute fabric in unsaturated polyester resin. An improvement in the mechanical properties of laminates was observed when jute fabric was modified by titanate treatment.

1.13 BIODEGRADABLE JUTE FIBER COMPOSITES

There is a growing interest in the use of agro-fibres as reinforcing components for thermoplastics, because they are renewable, biodegradable and environmentally friendly. Again, the growing environmental concern has made plastics a target of criticism due to their lack of degradability. So there has been a lot of interest in research committed to the design of biodegradable plastics [196]. Biodegradable polymers are considered as an environmental waste-management option [197]. They constitute a loosely defined family of polymers that are designed to degrade through action of living organisms and they offer a possible alternative to traditional non-biodegradable polymers where recycling is unpractical or not economical. The management of solid waste disposal with regard to the decreasing availability of landfills, the litter problem and the pollution of marine environment are becoming very urgent in the industrial countries and risk to extend very quickly to the developing countries. Interest in biodegradable plastics is being revived by new technologies developed by major players, such as Bayer, DuPont and Dow Cargill [198]. Demands for biodegradables are forecast to grow nearly 16% per annum [199]. The manufacture, use and
removal of traditional composites, usually made of glass, carbon or aramid fibres reinforced thermoplastics and thermosetting resins are considered critically because of environmental problems. Natural fibre reinforced biodegradable matrix composites (biocomposites) will get much attention in the future [200]. Jute, the so-called golden fibre from eastern India and Bangladesh is one of the most common agro-fibres having high tensile modulus and low elongation at break. If the low density (1.4 g/cm$^3$) of this fibre is taken into consideration, then its specific stiffness and strength are comparable to the respective quantities of glass fibres [201]. There are many reports about the use of jute as reinforcing fibres for thermosets and thermoplastics [202].

1.14 PRESENT WORK

The research work described in the present thesis is mainly related to the elaborative aspects like studies on the synthesis of unsaturated polyester resin (UP), modification of unsaturated polyester resins and characterization by chemical methods and advanced instruments.

In the present study various unsaturated polyester resins were prepared by the reported method [26] using monomers like phthalic anhydride, maleic anhydride, and propylene glycol in different molar ratios, modified using adipic acid, fumaric acid and lactic acid. The composites were prepared for all modified unsaturated polyester resins by using jute fibers.

Chapter-1: Introduction

It includes the general introduction of polyester resin and its applications with references.

Chapter-2: Preparation and characterization of adipic acid modified polyester resin.
It contains the synthesis and characterization of unsaturated polyester (UP) resin using various monomers like phthalic anhydride, maleic anhydride and propylene glycol. The UP resins were modified using monomer like adipic acid with reactive diluents styrene and characterized by acid value, IR, TGA and DTA

**Chapter-3: Preparation and characterization of fumaric acid modified polyester resin.**

It contains the synthesis and characterization of unsaturated polyester (UP) resin using various monomers like phthalic anhydride, maleic anhydride and propylene glycol. The UP resins were modified using monomer like lactic acid with reactive diluents styrene and characterized by acid value, IR, TGA and DTA

**Chapter-4: Preparation and characterization of lactic acid modified polyester resin.**

It contains the synthesis and characterization of unsaturated polyester (UP) resin using various monomers like phthalic anhydride, maleic anhydride and propylene glycol. The UP resins were modified using monomer like fumaric acid with reactive diluents styrene and characterized by acid value, IR, TGA and DTA

**Chapter-5: Composite for speciality applications.**

The biodegradable composite preparation using polyester resin and modified polyester resin (60% by weight) are discussed in this chapter. The jute was used for preparation of composites. The composites were characterized by Rockwell Hardness, Izod Impact, Flexural Strength and Flexural Modulaus. The biodegradability of polyesters made composites were evaluated by enzymatic degradation test.
Chapter 6: Result and Discussion

In this chapter the unsaturated polyester resin and adipic acid, lactic acid & fumaric acid modified polyester resin & the jute composites results were discuss in detail. The all series result was discuss in detail and compared with each others.
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