CHARPTER 1

Introduction

Unsaturated polyesters (UP) are extensively used in glass-reinforced Composites in the automotive, marine, and infrastructure industries. They can provide excellent mechanical and chemical properties, good chemical and weather resistance with relatively low cost.

During compound curing, unsaturated polyesters (UP) resin molecules rearrange themselves to change from liquid phase to solid phase and density increases, which create volume shrinkage during compound curing. This high polymerization shrinkage, about 7-10%, which is created by free radical copolymerization of unsaturated polyester resin and styrene, creates problems in surface quality and dimension control.

1.1 Polymeric Composites

Composite materials are divided to several kinds such as metal composite, ceramic composite and polymeric composites based on used materials in composition.

Polymer composites are an important class of engineering materials which consist of two or several components. They are widely used in automotive, aerospace, construction, transportation, defense, recreational, sporting goods and electronic applications, replacement of conventional materials because of their light weight, high strength to weight ratio, structural soundness, low cost and ease of moulding into
different shapes compared to conventional materials such as wood, metals, etc. They obtain better mechanical properties, higher fatigue strength, excellent corrosion resistance while their tooling cost is low comparing to conventional materials [Sheldon 1982, Bikales et al 1988].

Compared to pure polymeric materials, Polymer composites lead to corrosion resistance and exhibit better chemical or physical properties such as high strength and modulus, good dimensional stability and provide more flexibility in design for industrial products.

Because of various molecular structures and behaviors of polymer resins, there are two types of polymer resins, Thermoset resins and thermoplastic resins. Both thermoset and thermoplastic polymers can be employed to produce polymeric composites [Schwartz, 1996]. thermoset polymer resins by applying curing agent (heat or initiator) are crosslinked. The chemical reaction between resins polymer leads to create a three-dimensional network structure which makes polymer resins to change from liquid to solid and can not be reformed by using heat and pressure. That means, crosslinking of polymer resins is a non reversible process.

While thermoplastic resins are melted and formed in a linear structure without chemical linking between them and by applying of heat and pressure can be softened and re-formed. The process is reversible. But, today most composites manufacturers use thermoset polymers, because of their superior properties.

The commonly used thermoplastic resins systems include poly vinyl chloride (PVC), polyethylene (PE), polystyrene (PS), poly methyl methacrylate (PMMA), polycarbonate (PC), polypropylene (PP), polyamide (PA), etc.

The most common thermoset resins include epoxy, phenolic, unsaturated polyester, vinyl ester, polyurethane. Each of them has particular advantages or disadvantages that relates to its application.
The additives used to thermoset polymer composites are materials consisting of fillers in the form of inorganic, organic compound, which are designed to reduce the cost of composites and improve performance which cannot be provided by the reinforcements and polymer resins alone.

Generally, the most widely used component of polymeric composites is fibers which are also called fiber reinforced plastics. The most common fiber reinforcements used in polymeric composites are Kevlar fiber, glass fiber and carbon fiber.

Fiber reinforced polymeric composite is composed of a fiber reinforcement, a matrix resin and an interface between them. The matrix binds the reinforcements together and transmits load between the individual reinforcements and protects the reinforcements from environmental damage and humidity. The fibers increase strength and hardness of the composite structure while the interface allows transfer of load from the polymer matrix to the fiber reinforcements. In addition thermoset polymer composites exhibit superior properties which could not be provided by the reinforcements and polymer resins alone. The most widely used fiber reinforcements to polymeric composites are Kevlar fiber, glass fiber and carbon fiber.

One of the most commonly used thermoset resins throughout the world is unsaturated polyester (UP) resins. Their properties such as low viscosity, fast cure, excellent chemical resistance, coatings and cast objects. The simple processing, low cost, their ability to cure at room temperature and atmospheric conditions allows glass fiber reinforced plastics use in tanks, underground pipes, automobile and boat bodies [Updegraff 1982, Juska et al 1996, Penczek et al 2005]. Also comparing to other thermosetting resin unsaturated polyester resin have some advantage such as ability to use in the liquid form for filling and be reinforced with fiber, easy to handle and can be pigmented and the main disadvantage of unsaturated polyester resin is the high volumetric shrinkage on curing, which results in residual stresses.

Due to all discussed advantage of unsaturated polyester resin, there is rapid increase in the share of UP resins in the plastics market in recent years which is more than
85% of the total resins used in the thermoset composite material while unsaturated polyester resin used in 1999 was about 70% and in 1986 was about 60% [Bikales et al 1988, CFA1999].

Commercial unsaturated polyester resins include linear polyester with varying amount of unsaturated units and styrene monomer as a crosslinking monomer. Generally, reins contain 30-50 wt% styrene monomer by weight (depending on viscosity of resin and conditions of product processing) and inhibitors which prevent any cross-linking reaction prior to processing.

The common crosslinking monomer for the curing of unsaturated polyester resins is styrene because of it’s advantage such as high reactivity, high flexural and low cost comparing to another crosslinking monomers include divinyl benzene, methyl methacrylate, vinyl toluene. Additionally, styrene can be used for adjusting of unsaturated polyester’s viscosity because it also acts as a solvent for unsaturated polyester. Chlorendics and Bisphenol A fumarates as saturated diacids can be used to formulate polyester resins to get a special corrosion resistance in resins.

Other special polyesters are dicyclopentadiene (DCPD) which are used commonly in the boatbuilding industry. They have higher cost but they have fast and complete cure and also exhibit low shrinkage comparing to other polyesters resins during cure. on the other hand a few problems with these resins has been reported such as high rigidity and weak toughness comparing to other polyester resins which caused to blend with other polyester resins to improve the properties of DCPD resins.

Epoxy resins are another thermoset resins which are mainly used to produce composite with excellent electrical and mechanical properties, resistance to corrosive environment, good adhesion to many metals, low shrinkage and good performance at high temperatures. The drawback of epoxy resins include relatively high cost and long cure time which limit their use in high volume applications.

Vinyl ester resins are similar to polyesters in their molecular structure, but their reactive sites being positioned only at the ends of the molecular chains. Therefore
the whole length of the molecular chain is available to absorb shock loadings which can make vinyl ester resins tougher and more resilient than polyesters.

Comparing epoxy resins and polyester resins to Vinyl ester resins, Vinyl ester resins have low viscosity at room temperature and fast cure and relatively low cost which makes them easy to process in various molding processes. Although cost of vinyl ester resins is more than polyesters but their high degree of moisture resistance cause to used them mainly in chemically corrosive environments and structural laminates such as boat buildings and swimming pools structure.

Other common thermoset resins are polyurethanes which are produced by the reaction of polyol and polyisocyanat. Polyurethane resins have many advantages such as chemical, oil and grease resistance. They are typically excellent in resisting abrasion which causes to use to produce synthetic rubbers. Additionally, they can be used to create strong adhesives. They have some disadvantages such adversely affected by direct sunlight and generally do not hold up well when exposed to organic solvents. They are mostly used in the transportation products such as car seats, bumper beams and spare tire covers.

Calcium carbonate, kaolin and alumina hydrate are three main fillers used with polymer matrix in the composite industry. Fillers improve crack resistance and stiffness, control viscosity, shrinkage and also reduce cost [Mallick 1988, Penczek et al 2005]. Other filler used in the composite industry are clay, feldspar, mica, silica, glass micro-spheres, and micro-rubber balloon.

Also additives can be used to improve composite properties, applications, and appearance such as release agents, catalysts, flame retardants, inhibitors, and ultraviolet (UV) absorbers [Modern Plastics Encyclopedia, 1998]. However calcium carbonate is widely used to reduce the cost and mold shrinkage with unsaturated polyester.
The polymerization initiators used in unsaturated polyester resins and styrene monomer include: t-butyl hydro peroxide, t-butyl perbenzoate, benzoyl peroxide, methyl ethyl ketone peroxide. Initiator use is 0.3% - 2.3% by wt% based on the total component [Atkins, 1978]. Cobalt naphthalene and cobalt octoate act as accelerators, to reduce curing time.

Generally major applications of unsaturated polyester resins are: glass fiber laminates and molding compositions. The manufacturing method of fiber reinforced polymeric composite include compression molding of sheeting molding compound (SMC), hand lay-up, injection molding of bulk molding compound (BMC), vacuum bagging and autoclave curing, resin transfer molding (RTM), continuous pultrusion, continuous lamination and casting [Penn 1966, Mallick 1988]. But the most commonly used fabrication techniques for unsaturated polyester resins include vacuum bagging and autoclave curing, hand lay-up, continuous pultrusion, compression molding.

1.2 Unsaturated Polyester Resins

Polyesters are a large class of synthetic resins having widely varying properties. Polyester resin-based adhesives are relatively low cost formulations that have found niche applications. They may be divided into two distinctive groups: saturated (thermoplastic) and unsaturated (thermosetting) [Petrie, 2000].

Polyesters are also common thermosetting resins that are used in many applications such as automobile and boat parts, fiberglass structures, and molding compounds. Polyesters are generally heavily filled and/or contain reinforcing fibers such as glass. Polyester resins are somewhat lower in cost than epoxy resins and can be formulated to have very short molding times. They have good resistance to water, good electrical properties, good resistance to oils and solvents, and high strength-to-weight ratios [Petrie, 2000].
Unsaturated polyester laminating resins are viscous materials of a low degree of polymerization (i.e. oligomers) with molecular weights of 1500–3000 [Chanda and Roy, 2009].

They are prepared in a step polymerization process from a glycol, typically 1,2-propylene glycol (1,2-propanediol), together with both an unsaturated dicarboxylic acid (maleic acid) and a saturated carboxylic acid (phthalic or isophthalic acid).

Propylene glycol, 1,4-butanediol, neopentyl glycol, diethylene glycol, and bisphenol A are also used in place of ethylene glycol as the diol component. Aromatic reactants are used in the formulation to improve the hardness, rigidity, and heat resistance of the crosslinked product. Halogenated reactants are used to impart flame resistance [Odian, 2004].

General purpose resins generally employ either maleic acid (usually as the anhydride) or its trans-isomer fumaric acid as the unsaturated acid:

![Figure 1.1: Some example of unsaturated acid structure [Chanda and Roy, 2009].](image-url)

Maleic anhydride or fumaric acid confers the fundamental unsaturation to the polyester which provides the reactivity with coreactant monomers such as styrene. Maleic anhydride is a crystalline solid melting at 52.6°C (the acid melts at 130°C), while fumaric acid is a solid melting at 284°C. The latter is sometimes preferred to
maleic anhydride because it is less corrosive, tends to give lighter colored products, higher impact strength, and slightly greater heat resistance.

Phthalic anhydride (melting point 131°C) is most commonly used to play the role of the saturated acid because it provides an inflexible link and maintains the rigidity in the cured resin. It is also preferred because its low price enables cheaper resins to be made. Use of isophthalic acid (melting point 347°C) in place of phthalic anhydride yields resins having higher heat distortion temperature and flexural moduli, better craze resistance, and often better water and alkali resistance. These resins are also useful in the preparation of resilient gel coats. Where a flexible resin is required, adipic acid may be used since, unlike the phthalic acids which give a rigid link, adipic acid gives highly flexible link and hence flexibility in the cured resin. Flexible resins are of value in gel coats [Chanda and Roy, 2009].

Polyesters formed from phthalic anhydride and glycerol was among the first commercial crosslinked polyesters. Linear polyesters seldom are synthesized by the direct reactions of acids or acid anhydrides with alcohols because the higher temperatures required for high conversions lead to side reactions, which interfere with obtaining high molecular weights. This consideration is not overwhelmingly important for crosslinking systems, since crosslinking is achieved at far lower extents of reaction than are needed to obtain high polymer in a linear polymerization. Crosslinked polyesters are typically synthesized by direct esterification of acid or acid anhydride with alcohol [Odian, 2004].

Figure 1.2: Some example of saturated acid structure [Chanda and Roy, 2009].
Simple polyesters of the type described by equation (1.1) are too limited to be of commercial interest. Almost all crosslinked polyesters are either unsaturated polyesters or alkyd polyesters. These offer a greater ability to vary the final product properties to suit a targeted market. Also, they offer greater process control since different chemical reactions are involved in the polymerization and crosslinking reactions. Typical unsaturated polyester is that obtained by the polymerization of maleic anhydride and ethylene glycol. Maleic anhydride is only a bifunctional reactant in the polyesterification reaction, but it has the potential for a higher functionality under the appropriate reaction conditions [Odian, 2004].

\[
\begin{align*}
\text{OC} & \text{O} \quad \text{CO} + \quad \text{CH}_2\text{OH} \\
\text{CH}_2\text{OH} & \quad \text{CH} \quad \text{CHOH} \\
\text{CH}_2\text{OH} & \quad \text{CH} \quad \text{CHOH} \\
\end{align*}
\]

(1.1)

The alkene double bond is reactive under radical chain polymerization conditions. Crosslinking is accomplished in a separate step by radical copolymerization with alkene monomers such as styrene, vinyl toluene, methyl methacrylate, triallyl cyanurate, and diallyl phthalate.
Generally, interested unsaturated polyester resins in composite industry are step-growth polymers formed by condensing a alcohols with both an unsaturated acids or anhydrides and saturated acids. The unsaturated acid is usually maleic anhydride and saturated acid is phthalic anhydride or isophthalic acid. The saturated acid provides unsaturated carbon-carbon (C==C) double bonds as a site for cross linking between polymer chains with vinyl monomers (such as styrene) and make three-dimensional network structure while The purpose of the saturated acid is to reduce the number of sites for cross linkage which in turn reduces brittleness of the final product. The main chemical specie for unsaturated polyester resins is glycol such as ethylene glycol, propylene glycol which is used to make unsaturated polyester resins. A typical example for the unsaturated polyester resins synthesis is shown in Equation (1.3) [Bruins, 1976]. The viscous polyesters are dissolved in styrene monomer (30–50% concentration) to reduce the viscosity [Chanda and Roy, 2009].

Equation (1.3) Example of the reaction mechanism of unsaturated polyester resin [Bruins, 1976].
Depending on the structure acid included in the resins, unsaturated polyesters can be divided into different classes: orthophthalic, isophthalic, and other specialty polyesters.

The unsaturated polyester resins based orthophthalic acid as the saturated acid is called orthophthalic resins which are also known as general-purpose resins. Although their cost is low comparing to other polyester resins but their poor corrosive resistance, partly because of the residual organic compounds in orthophthalic resin and the lower molecular weight [Ghotra et al, 1975] has been caused to limit their applications. They are commonly used in the some applications which the corrosion resistance is not the major concern for them. The isophthalic acid based unsaturated polyester resins are called isophthalic resins which are also known as premium resins. Although they have higher cost comparing to orthophthalic resin but their better mechanical properties, corrosive resistance, heat resistance, toughness [Burns, 1982] made to use them in more applications. Generally, Isophthalic resins have higher molecular weight than orthophthalic resins which require more contents of styrene monomer in formulation.

Table 1.1 shows a summary of building blocks of unsaturated polyester resins and their contributions [Trivedi et al, 1982].

Generally unsaturated polyesters have a good combination of resistance to softening and deformation at high temperature, electrical properties, resistance to corrosion, weak alkalies, and strong acids and possess very good weatherability. The liquid polyester prepolymeres are especially easy to fabricate into infusible thermoset objects by casting in open molds, spray techniques as well as compression, hand layup, and resin-transfer molding. Unsaturated polyesters are used extensively in the construction (tub and shower units, building facades, specialty flooring, cultured onyx and marble, chemical storage tanks), transportation (truck cabs, auto body repair), and marine (boat hulls) industries as well as for business machine and electric handtool molded parts [Odian, 2004].
### Table 1.1: Unsaturated polyester building blocks [Trivedi et al, 1982].

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<th>Building Blocks</th>
<th>Ingredients</th>
<th>Characteristics</th>
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| Unsaturated anhydrides and dibasic acids | 1. Maleic anhydride  
2. Fumaric acid | 1. Lowest cost, moderately high heat deflection temperature (HDT)  
2. Highest reactivity (cross-linking), higher HDT, more rigidity |
| Saturated anhydrides                     | 1. Phthalic (orthophthalic) anhydride  
2. Isophthalic  
3. Adipic acid, azelaic acid, and sebacic acid  
4. Chlorendic anhydride HET anhydride  
5. Nadic methyl anhydride  
6. Tetrachlorophthalic anhydride  
7. Tetrabromophthalic anhydride | 1. Lowest cost, moderately high HDT, provides stiffness, high flex, and tensile strength  
2. Higher tensile and flex strength, better chemical and water resistance  
3. Flexibility (toughness, resilience, impact strength); adipic acid is lowest in cost of flexibility acids  
4. Flame retardance  
5. Very high HDT  
6. Flame retardance  
7. Flame retardance |
| Glycols                                  | 1. Propylene glycol  
2. Dipropylene glycol  
3. Ethylene glycol  
4. Diethylene glycol  
5. 2,2,4-Trimethyl-1,3-pentanediol glycol  
6. Bisphenol-A adduct  
7. Hydrogenated bisphenol-A adduct  
8. Tetrabromobisphenol-A | 1. Lowest cost, good water resistance and flexibility, compatibility with styrene  
2. Flexibility and toughness  
3. High heat resistance, tensile strength, low cost  
4. Greater toughness, impact strength and flexibility  
5. Corrosion resistance with reduced density  
6. Corrosion resistance, high HDT, high flex and tensile strength  
7. Corrosion resistance, high HDT, high flex and tensile strength  
8. Flame resistance |
One of especial unsaturated polyester resins (UPRs) with enhanced chemical, thermal and mechanical resistance were synthesized from neopentyl glycol as main chemical specie for unsaturated polyester resins and isophthalic acid. The properties of isophthalic-neopentyl resins and the commercial ortho-phthalic resin were compared. The resin based on neopentyl glycol was characterized by higher impact and flexural strength as well as higher chemical and thermal resistance [Penczek et al, 2005].

1.3 Crosslinking Mechanism of UP Resin

In order to bring about crosslinking of polyesters with styrene several type of initiator systems is used, which differ in Radicals production methods include thermal, photochemical, and redox methods [Odian, 2004] which they are effective. The thermal, homolytic dissociation of initiators is the most widely used mode of generating radicals to initiate polymerization–for both commercial polymerizations and theoretical studies. Polymerizations initiated in this manner are often referred to as thermal initiated or thermal catalyzed polymerizations. There are number of different types of compounds that can be used as thermal initiators. However, it is the peroxides which find extensive use as radical sources. The other classes of compounds are usually either not readily available or not stable enough [Odian, 2004]. Among those peroxides employed are benzoyl peroxide, t-butyl perbenzoate, 2,4-dichlorobenzoyl peroxide, di-t-butyl peroxide, and dodecyl peroxide. Mixtures of polyester prepolymer, styrene and such initiators are reasonably stable at room temperatures but undergo fairly rapid crosslinking at temperatures between 70 °C and 150 °C, depending on which particular peroxide is used. The thermal, homolytic dissociation of initiators is the most widely used mode of generating radicals to initiate polymerization–for both commercial polymerizations and theoretical studies. The initiation step is considered to involve two reactions. The first is the production of free radicals by any one of a number of reactions. The usual case is the homolytic dissociation of an initiator species I to yield a pair of radicals R•.
\[
I \xrightarrow[K_d]{\text{K}_d} 2R^\cdot \quad (1.4)
\]

Where \( K_d \) is the rate constant for the catalyst dissociation. The second part of the initiation involves the addition of this radical to the first monomer molecule to produce the chain initiating radical \( M_1^\cdot \), where \( M \) represents a monomer molecule and \( K_i \) is the rate constant for the initiation step [Odition, 2004].

\[
R^\cdot + M \xrightarrow[K_i]{\text{K}_i} M_1^\cdot \quad (1.5)
\]

Several different types of peroxy compounds are widely used which undergoes the kind of reactions illustrated in generating radicals shown in equations 1.6, 1.7 and 1.8. [Odition, 2004].

benzoyl peroxide:

\[
\begin{align*}
\phi-C-O-O-C-\phi & \quad \rightarrow \quad 2\phi-C-O^\cdot
\end{align*}
\quad (1.6)
\]

di-t-butyl peroxide:

\[
\begin{align*}
\text{H}_3\text{C}-\text{C}-\text{O}-\text{O}-\text{C}-\text{C}_3 & \quad \rightarrow \quad 2\text{CH}_3\text{C}-\text{O}-\cdot
\end{align*}
\quad (1.7)
\]

t-butyl perbenzoate:

\[
\begin{align*}
\phi-C-O-O-C-\text{C}_3 & \quad \rightarrow \quad \phi-C-O^\cdot + \text{O}-C-\text{C}_3
\end{align*}
\quad (1.8)
\]

Some of peroxide initiators for a number of applications curing at room temperature are desirable. This so-called ‘cold cure’ is brought about by using a peroxy initiator in conjunction with some kind of activator substance. The peroxy compounds in these
cases are substances such as methyl ethyl ketone peroxide and cyclohexanone peroxide, which as used in commercial systems tend not to be particularly pure, but instead are usually mixtures of peroxides and hydroperoxides corresponding in composition approximately to that of the respective nominal compounds. Activators are generally salts of metals capable of undergoing oxidation/reduction reactions very readily. A typical salt for this purpose is cobalt naphthenate, which undergoes the kind of reactions illustrated in Reactions 1.9 and 1.10.

\[
\text{ROOH} + \text{Co}^{2+} \rightarrow \text{RO}^\cdot + \text{OH}^- + \text{Co}^{3+} \quad (1.9)
\]

\[
\text{ROOH} + \text{Co}^{3+} \rightarrow \text{ROO}^\cdot + \text{OH}^- + \text{Co}^{2+} \quad (1.10)
\]

Cold-cure crosslinked polyester resins are used extensively in the production of large glass-fibre reinforced items, which are usually made by the hand lay-up technique.

The crosslinking of unsaturated polyesters is carried out by copolymerization [Odian, 2004]. Low-molecular-weight unsaturated polyester (prepolymer) and radical initiator are dissolved in a monomer, the mixture poured, sprayed, or otherwise shaped into the form of the desired final product, and then transformed into a thermoset by heating. Styrene is the most commonly used monomer. Vinyltoluene, methyl methacrylate, diallyl phthalate, a-methylstyrene, and triallyl cyanurate are also used; often together with styrene. The crosslinking process involves copolymerization of the added monomer with the double bonds of the unsaturated polyester [Odian, 2004].

The mechanical properties of the crosslinked product depend on the average number of crosslinks between polyester chains (crosslink density) and the average length of the crosslinks.

The crosslink density depends on the relative amounts of saturated and unsaturated acids used in synthesizing the prepolymer. The average length of the crosslinks
depends not only on the relative amounts of prepolymer and monomer but also on the copolymerization behavior of the two double bonds. Thus for a polyester containing fumarate double bonds crosslinking by copolymerization with styrene yields a harder and tougher product than when methyl methacrylate is used. The fumarate–styrene system shows more of an alternating copolymerization behavior than does the fumarate–methyl methacrylate system.

Methyl methacrylate tends to form a small number of long crosslinks (large value of \( n \) in Equation 1.11), while styrene forms a larger number of short crosslinks (small value of \( n \)). Allyl monomers such as diallyl phthalate are useful for producing high densities of short crosslinks due to degradative chain transfer.

\[
\begin{align*}
\sim \text{O}_2\text{C} \sim \text{CH} \equiv \text{CH} \sim \text{CO}_2 \sim + \text{CH}_2 \equiv \text{CH} \equiv \text{A} & \rightarrow \\
\sim \text{O}_2\text{C} \sim \text{CH} \sim \text{CH} \sim \text{CO}_2 \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \text{O}_2\text{C} \sim \text{CH} \equiv \text{CH} \sim \text{CO}_2 \sim & \\
\text{(CH}_2 \equiv \text{CH}_2 \equiv \text{A}) \sim & \\
\sim \text{O}_2\text{C} \sim \text{CH} \equiv \text{CH} \sim \text{CO}_2 \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \text{O}_2\text{C} \sim \text{CH} \equiv \text{CH} \sim \text{CO}_2 \sim & \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim \sim 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Figure 1.3: Curing of unsaturated polyesters. (a) Species in polyester resin ready for laminating. (b) Structures present in cured polyester resin. Cross-linking takes place via an addition copolymerization reaction. The value of n=2–3 on average in general-purpose resins [Chand and Roy, 2009].
1.3.1 Microgel Formation

In the free-radical polymerization of vinylic monomers, gel is formed if the following conditions are fulfilled: (1) a mechanism leading to long-chain branches (LCBs) is operative, for example chain transfer to polymer, and (2) a mechanism that links polymer chains is also operative, for example termination by combination or propagation to pendent double bonds. Obviously, if multifunctional monomers are homopolymerized or copolymerized with vinylic monomers, gel is also formed. In this case, the predominant reaction linking polymer chains and leading to polymeric networks is the propagation to pendent double bonds of the multifunctional monomers. Under these circumstances, polymer chains of increasing density of branching and crosslinking are formed and their molecular weight will rapidly increase, leading to the formation of gel polymer [Meyer et al, 2005].

Microgel-based mechanisms were proposed for the curing reactions. It was found that for high-temperature reactions the styrene content and the reaction temperature would affect the formation of the microgel structure and would affect participation of the intramicrogel and intermicrogel crosslinking reactions. For the medium-temperature reactions with the promoter-accelerated initiator systems, a predominance of intramicrogel reactions in the early stage of crosslinking was postulated. The higher molar ratio of styrene to polyester C==C bonds increases the favorable styrene swelling effect and enhances the intramicrogel reactions, but the degree of C==C unsaturations of UP resins has less significant effects on the curing time and the cure characteristics.

The formation of a heterogeneous structure through intramolecular reactions and the phase separation process being typical for free-radical crosslinking copolymerization of UP resins with styrene was studied. It was found that phase separation started right after the primary polymers were formed, if the resin system had moved into the two-phase region. The characteristics of the primary polymers agreed well with the description of the microgels and the microgels remained unchanged before phase separation and gelation. During the phase separation or when the reaction was
approaching gelation, secondary intramolecular reactions and interparticle reactions of microgels were observed. The phase separation process stopped after the resin reached its gel point, and the domain size of the separated phase remained the same throughout the rest of the reaction period. The morphological changes affect not only the cure behavior and rheological changes of the resin, but also the physical properties of the final products. Secondary intramolecular and interparticle reactions increased the styrene content in the polymer chain and the vinylene conversion [Penczek et al, 2005].

1.4 Unsaturated Polyester Production Problem

Unsaturated polyester resins are viscous materials and produced by mixing a glycol with both an unsaturated acid (maleic anhydride) and a saturated carboxylic acid (phthalic or isophthalic acid) with average number of molecular weights about 1500 to 3000. They are dissolved in styrene monomer (30-50 %wt) to reduce the viscosity of polyester resins. In the curing of unsaturated polyester (UP) resins, the volume shrinkage about 7-10% is major problem in unsaturated polyester resin production [Dong et al 2005, Chand and Roy2009].

During compound curing, unsaturated polyesters (UP) resin create three dimensional networks structure by free radical copolymerization with a vinyl monomer, i.e., styrene in resin mixture which causes to change resins from liquid phase to hard thermoset solid and its density increases, which lead to create volume shrinkage during compound curing. It has the strongest effect on the surface quality. They are usually crosslinked at an elevated temperature or at room temperature with related combination of initiators to curing temperature.
But increasing the cure temperature result in higher degree of cure and more compact in resins structure which in turn exhibit higher volume shrinkage in cured samples, while increasing fillers can reduce volume shrinkage [Melby 1989, Hill Jr et al 1995]. The fillers are typically inert and could not affect chemically in resin system, therefore using filler cause to reduce crosslinking density leads to better shrinkage control. Although adding fillers and fibrous reinforcement can reduce the volume shrinkage, but cannot completely eliminate shrinkage [Melby 1989, Hill Jr et al 1995].

During polymerization, the volumetric changes include two phenomena: cure shrinkage and thermal expansion/contraction. To better understand these phenomena, Li et al [2004] suggested a simple schematic representation of volume change of thermoset resins during cure (Figure 1.4). While it was designed for volume change of epoxy resins, it also applies to polyester resins.

Step a-b: By increasing temperature to start cure, the resin volume increases because of thermal expansion.

Step b-c: during isothermal cure, curing shrinkage cause to volume decrease.

Step c-e: during cooling to room temperature, the thermal contraction cause to volume decreases.
However the volume shrinkage during curing of resin compound has more effect than its thermal expansion which in turn cause to surface defects such as ripples, fabric print through, and dimensional inaccuracy which limit the growth of many high-volume applications.

- Surface defects, including surface waviness and fiber pattern readout.
- Warpage and dimension inaccuracy of cured samples.
- Internal cracks and voids in thick sections.
- Sink mark on the appearance surface opposite to reinforced ribs or bosses.
Some helpful techniques to correcting the surface defect and dimensional accuracy such as putty and sanding can be used to improve surface quality and remove the damage areas from part surface but those methods are expensive and cannot thoroughly eliminate the surface defects. Other technique to correcting the surface defect and reduce volume shrinkage is re-injection of resin into the mold at the final stage of curing which is used specially in mold coating mostly in SMC molding. In this method re-injection of resin into the mold cause to makes a resin layer which can cover all the surface defects caused by polymerization shrinkage and improve surface quality results in reduce shrinkage [Bartkus, et al 1970, Kia 1989]. But these methods are costly and also cannot solve surface defects problem completely.

It was finally found that adding Thermoplastic materials as low profile additives (LPAs) have been very effective in controlling volume shrinkage of cured UP resins [Pattison et al 1974 and 1975, Bucknall et al 1985, Lucas et al 1993, Li et al 2000]. Thermoplastic materials as low profile additives (LPAs), effectively control volume shrinkage of cured UP resins. They are thermoplastic particles that become incompatible with the resin molecules during cure causing phase separation and inversion between the LPA-rich and resin-rich phase, and creating the micro-voids at the inside or interface the LPA-rich phase can to control the resin shrinkage during curing and cooling.

LPA has been found to be highly effective in controlling the curing shrinkage of UPE resins in high-temperature moulding processes such as compression moulding of sheet moulding compounds (SMCs) and injection moulding of bulk moulding compounds (BMCs).
Chapter 1

1.5 Scope of Study

The objective of this study is an integrated analysis of effect of nanoclay on the volume shrinkage control, reaction kinetics, morphology and mechanical properties of cured unsaturated polyester resin.

The scope of the work is described as follows:

Chapter 2 is a literature review of low profile additives and their effective factors on shrinkage control, their properties and mechanisms, and finally nanoparticles and nanofibres.

Chapter 3 covers the detailed study and experimental on effect of low profile additives and nanoclay on shrinkage control of unsaturated polyester resin by using density measurement method. The experimental is done on samples with different molecular weight of Low profile additives and different nanoclay in different cure temperature. At the end of this chapter, data values of shrinkage for different content value of PMMA and nanoclay in UP resin is used to obtain correlation equations to predict the shrinkage value for cure at room temperature or in high temperature.

Chapter 4 uses scanning electronic microscope (SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), universal testing machine and impact tester to describes the effect of nanoclay on shrinkage control of cured low profile unsaturated polyester (UP) resin by studying the samples morphology, clay partition, reaction kinetics and mechanical properties. Also the effect of different curing agent on morphology and kinetic rate in samples using nanoclay is investigated.

Chapter 5 concludes our work and some recommendations are outlined in this chapter.