CHAPTER I

INTRODUCTION

1.1 Unsaturated Polyester Resin (UPR)

An unsaturated polyester resin usually contains a polymerizable vinyl monomer and unsaturated polyester, which is prepared from a glycol and dibasic acids. The linear chain unsaturated polyester is dissolved in vinyl monomer, usually styrene, and the resulting resin is called an unsaturated polyester resin. This resin can be cured by the use of catalysts to yield hard insoluble thermoset polyester.

The commercial production of unsaturated polyester resins was started during World War II for military aircraft. Typically unsaturated polyester resins in their commercial form are mixtures of unsaturated polyester with styrene. The ratio of the unsaturated polyester to styrene monomer is usually varied to obtain the diverse applications. (1-3)

1.2 Materials

The variations can be made in the composition of the unsaturated polyester to yield the resins with a wide range of properties before, during and after polymerization. The main variables are the type and amount of dibasic acids, alcoholic vinyl monomers, molecular weights of the polyester resins and the inhibitor system.

1.2.1 Glycols

Propylene, diethylene, and dipropylene glycols are generally used in the commercial unsaturated polyester resin manufacture. Others less employed glycols are ethylene glycol, neopentyl glycol and hydrogenated bisphenol A. Propylene glycol is used in general purpose resins since it gives a high degree of compatibility with the vinyl monomers. Diethylene glycol can be used when greater resilience or flexibility is desired.

1.2.2 Unsaturated Acids

Most resins are made up of at least two dibasic acids. In a mixed acid composition, the lower ratio of unsaturated acid gives more flexible copolymers and slower curing time.

Maleic anhydride is mainly used for the unsaturated polyester resins. Fumaric acid, tetrahydrophthalic anhydride and carbic acid can also be used.

1.2.3 Saturated Acid

The simple polyester resins are made from a glycol and an unsaturated dibasic acid or anhydride. The high crosslinking density leads to extremely brittle, copolymers along with high heats during copolymerization. Saturated dibasic acids are used to improve the mechanical properties of the product. The most common saturated acids are phthalic anhydride, isophthalic acid and adipic acid.

Phthalic anhydride is the most widely used. The most common unsaturated polyester is synthesized from propylene glycol, maleic anhydride and phthalic anhydride. Phthalic anhydride contributes to a decrease of water absorption, improvements of the physical properties, increased compatibility with styrene and a lower cost. However, it is difficult to prepare high molecular weight polyester with phthalic anhydride since it has a strong tendency to reform from phthalic acid half esters. Isophthalic acid is free of this limitation and higher molecular weights polyesters can be prepared. Isophthalic polyesters also have excellent compatibility with styrene. In comparison to phthalic anhydride resins, isophthalic resins show better strength, toughness and increased heat and chemical resistance.

1.2.4 Monomers

Vinyl monomers are used to copolymerize with the unsaturation units in linear polyesters in order to develop the cross-linked or thermoset structure. Before this cross-linking or curing stage these monomers also serve as solvent for the high viscosity polyesters.

Styrene is the monomer of choice in most of unsaturated polyester resins. Vinyl toluene, methyl methacrylate, methyl acrylate, α-methylstyrene, diayl phthalate and triallyl cyanurate are less often used. The ideal monomers for unsaturated polyester resins should have high boiling point and low viscosity. The reactivity with the unsaturated polyesters should be high but has to be controllable. Styrene meets these requirements better than other monomers. Variations in the ratio of styrene to unsaturated groups in the polyester affect the physical strength, chemical resistance and electrical properties of the resulting copolymer. Styrene is generally used in the range of 35 to 45 wt % of the unsaturated polyester resin.

Vinyl toluene is widely used in the applications where lower vapor pressure and higher rate of polymerization are required. α-Methylstyrene is added in small amounts with styrene to extend the cure time and lower the exotherm of large castings. Methyl methacrylate and methyl acrylate are used together with styrene to improve light stability and weathering resistance. However, when only these acrylate monomers are used as the crosslinking monomer, their poor reactivity towards polyester chain lead to slow curing. The major applications of these monomers are in corrugated sheeting. Triallyl cyanurate are used with unsaturated polyesters where high temperature resistance is desired.

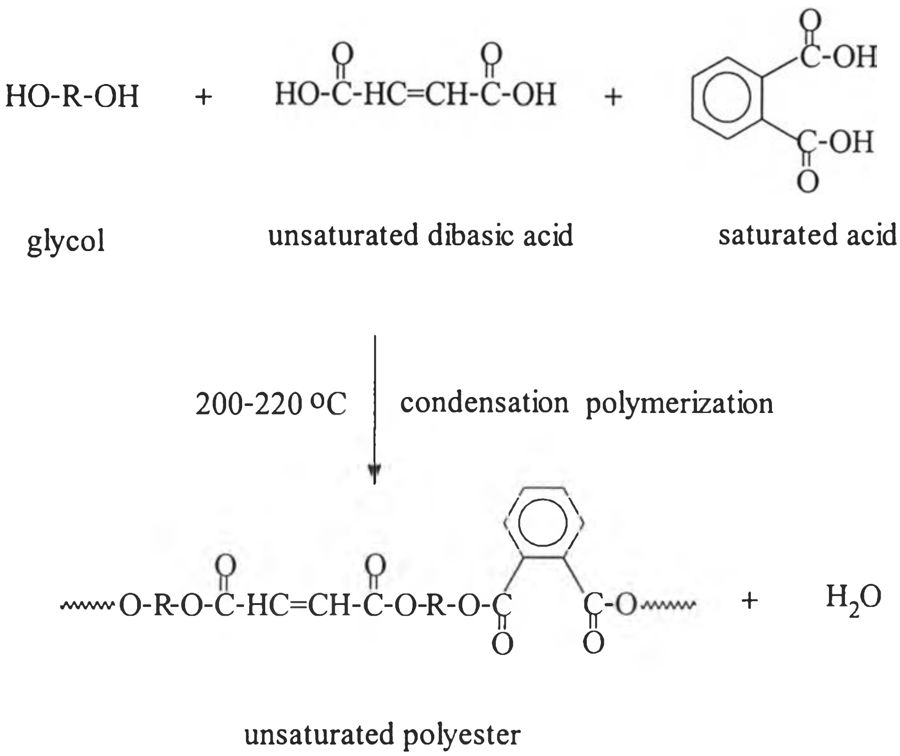
1.2.5 Inhibitors

The unsaturated polyester resins are highly reactive, since the heat, light and contamination can start the curing. The inhibitor system is an extremely important part of a polyester resin. It contributes storage stability to the resins and regulates the pot life and gel time after free radical initiators have been added to the resins. (1-4)

1.3 Preparation of Unsaturated Polyester

Unsaturated polyesters are usually prepared from a polycondensation reaction at elevated temperature between glycols and dibasic acids or anhydrides as shown in Scheme 1.1.

Depending on the types of glycols and acids, the unsaturated polyester is a linear polymer with a molecular weight ranging from about 700 to 20000. They are prepared in large reactors with overhead equipment designed to reduce the loss of volatile components. The acid value or a combination of acid value and viscosity of the polyester determines the end point of polyesterification reaction. After the unsaturated polyester has been prepared, it must be inhibited and diluted with vinyl monomer.



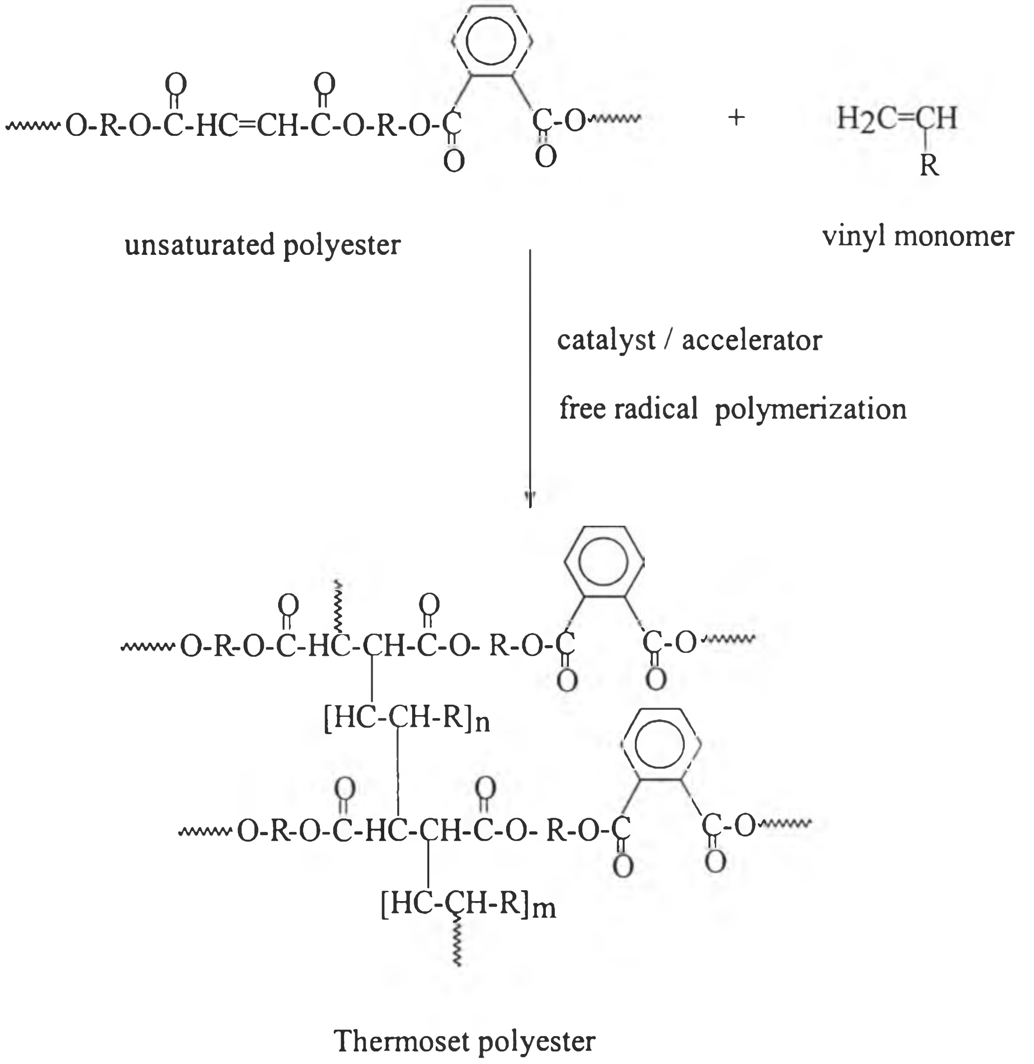
Scheme 1.1 Preparation of unsaturated polyesters

1.4 Curing (Copolymerization)

Methyl ethyl ketone peroxide is the most widely used of the low-temperature peroxide (20-60^{o}C) initiators. Benzoyl peroxide is the most popular of the medium-temperature peroxides (60-120^{o}C). Tertiary butyl perbenzoate and dicumyl peroxide are widely used in moulding systems that require temperature in range of 120-150^{o}C.

An accelerator is sometimes used to react with the peroxide to generate free radicals at a lower temperature. Metals and tertiary amine are the accelerators that are widely used.

The curing of unsaturated polyester resin is a free radical polymerization is shown in Scheme 2. To date, there are many studies involving the curing reaction and kinetics by the use DSC. (6-10)



Scheme1.2 Preparation of a thermoset polyester

1.5 Literature Survey

Rodriguez (11) investigated the effect of reactive monomers and functional polymers on the mechanical properties of a thermoset unsaturated polyester. The unsaturated polyester with 2:1 mole ratio of styrene to polyester unsaturation was modified with three vinyl monomers and two hydroxyl terminated polybutadienes. The three monomers used were 1,3 Butylene glycol dimethacrylate, tetraethylene glycol trimethylacrylate and trimethylpropane trimethylacrylate. Two hydroxyl terminated polybutadienes used were poly BD-R-45Ht and poly BD-R-45M. The results indicated that an increase in the crosslinking density resulted in deterioration in the tensile and flexural strengths.

Delcaba, Guerrero, Eceiza, and Mondragon (12) investigated the crosslinking process by static and dynamic viscosmetry and by differential scanning calorimetry. The different catalyst amounts added to the unsaturated polyester resin did not change the glass transition temperature. Nevertheless, an increase in catalyst concentration resulted in a decrease in gelation time. However, the difference in gelation time became smaller as the catalyst concentration was increased.

Many studies involved the cure of unsaturated polyesters by variation of catalyst type and concentration.(13-16) Huang and Chen (17) studied the effect of comonomer composition on the curing kinetics of unsaturated polyester resins by DSC and IR. Two commercial UP resins, UP2821 and UP536B, which contained 6.82 and 4.16 unsaturated C=C bonds per polyester molecule, respectively. The DSC rate of UP536B exhibited a shoulder after the peak which it could be caused by the grafting reaction of styrene on C=C bonds of the polyester chain inside the microgel particle.

Froehling (18) studied the combination of vinylesters and methacrylates in the crosslinking of unsaturated polyester resins. The polyester cured by the combination of these monomers gave materials with increased stiffness and strength in relation to those obtained with the separate monomers.

Other researchers (19-22) studied the modification of unsaturated polyester resins by adding poly(methyl methacrylate) or poly(vinyl acetate) to reduce the shrinkage of unsaturated polyester resin. The change in the properties of unsaturated polyester resins by the addition of blend materials such as poly(ethylene oxide), epoxy resin or filler was also investigated.(23-25)

1.6 Research Objectives

Unsaturated polyester resin has received increasing attention from industry, especially automotive industry. The properties of unsaturated polyester resins, which are factors in their successful applications, are corrosion resistance, lightweight, good physical properties and ease of color modification. In addition, resins can be formulated with good electrical resistance and other special characteristics such as heat and chemical resistance. In order to improve the properties of unsaturated polyester, other ingredients such as vinyl monomers are added.

It is known that addition of methyl methacrylate to the unsaturated polyester resins can increase the weathering resistance of the corresponding thermoset polyesters. The aim of this thesis is to study the effect of methyl methacrylate on the properties of unsaturated polyester resins and mechanical properties of their corresponding thermosets. This study also finds the optimum ratio of methyl methacrylate to styrene monomer in unsaturated polyester resins that provides the best mechanical properties in the thermoset polyesters.

Scope of the Research

1. Preparation of orthophthalic and isophthalic unsaturated polyester resins with different ratios of UP : SM : MMA

2. Characterization of unsaturated polyester resins in order to study the relationship between the properties of unsaturated polyester resins and weight ratio of UP : SM : MMA.

3. Investigation of the mechanical properties of the thermoset polyesters in order to study the relationship between the mechanical properties of thermoset polyesters and weight ratio of UP : SM : MMA at different % v/wt of MEKPO

4. Determination of the suitable compositions for the preparation of thermoset polyesters.