

**SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF THE
NEW UNSATURATED POLYESTER RESINS FOR COMPOSITE
APPLICATIONS**

by

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CHN	Carbon, Hydrogen, Nitrogen
DMSO-d ₆	Deuterated Dimethyl Sulphoxide
DSC	Differential Scanning Calorimetry
EFB	Empty Fruit Bunches
FRP	Fiber Reinforced Plastic
FT-IR	Fourier Transform Infrared
HDPE	High Density Polyethylene
¹ H-NMR	Nuclear Magnetic Resonance
KBr	Potassium Bromide
MEKP	Methyl Ethyl Ketone Peroxide
OD	Oven Dry
OPEFB	Oil Palm Empty Fruit Bunches
OPF	Oil Palm Fronds
OPT	Oil Palm Trunk
PBT	Polybutylene Terephthalate
PET	Polyethylene Terephthalate
PU	Polyurethane
TGA	Thermogravimetric Analysis
TMS	Tetramethylsilane
UHMW-PE	Ultrahigh molecular weight poly (ethylene)
UP	Unsaturated Polyester

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Proceedings and Presentation at 8th Pacific RIM Bio-Based Composites Symposium , 20-23 November 2006, Legend Hotel, Kuala Lumpur. M. Noorshashillawati Azura, H.P.S Abdul Khalil, A.M. Issam. New Unsaturated Polyesters with Different Lengths of Methylene Spacers for Composite Applications.	138
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M. Noorshashillawati Azura ¹ , H.P.S Abdul Khalil ^{1*} , A.M. Issam ¹ , M.R. Said ² , T.O. Mohd Adawi ³ , R. Ridzuan ⁴ . Oil Palm Empty Fruit Bunches (OPEFB) Reinforced in New Unsaturated Polyester Composites. Journal of Applied Polymer Science (In Press)	140
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SINTESIS, PENCIRIAN DAN SIFAT-SIFAT RESIN POLIESTER TAK TEPU BARU UNTUK APLIKASI KOMPOSIT

ABSTRAK

Pada masa ini, resin poliester tak tepu ialah matriks yang sangat penting dalam komposit polimer termoset. Objektif utama kajian ini adalah untuk mensintesis dan mencirikan poliester tak tepu baru untuk aplikasi komposit. Dua jenis poliester tak tepu disintesis daripada monomer *Bis-(2-hydroxyethyl) fumarate* (I) dan *Bis-(6-hydroxyhexyl) fumarate* (II). *Bis-(2-hydroxyethyl) fumarate* (I) dan *Bis-(6-hydroxyhexyl) fumarate* (II) disintesis daripada etilena glikol dan 1,6-heksanadiol dengan fumarik asid dalam kehadiran p-toluena sulfunik asid sebagai mangkin. Struktur kimianya disahkan dengan menggunakan analisis CHN, spektroskopi FT-IR dan spektroskopi ¹H-NMR. Sintesis poliester tak tepu baru diteruskan dengan tindak balas kondensasi antara *terephthaloyl chloride* dengan monomer I dan II. Struktur kimianya disahkan dengan menggunakan analisis CHN, FT-IR, ¹H-NMR spektroskopi, analisis termagravimetrik (TGA) dan analisis kalorimetri pengimbas pembezaan (DSC). Komposit diperkuat gentian tandan buah kelapa sawit kosong (OPEFB) dihasilkan daripada poliester tak tepu disediakan. Sifat mekanikal dan fizikal komposit diperkuat gentian OPEFB seperti kekuatan tensil, kekuatan fleksural, kekuatan hentaman dan penyerapan air turut dikaji. Secara umumnya komposit poliester baru diperkuat gentian OPEFB memperlihatkan sifat mekanikal yang paling tinggi jika dibandingkan dengan komposit poliester komersial diperkuat gentian OPEFB.

SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF NEW UNSATURATED POLYESTER RESINS FOR COMPOSITE APPLICATIONS

ABSTRACT

Currently the unsaturated polyester resin is an important matrix resins for thermosetting polymer composites. Major objectives of this study were to synthesis and characterize new unsaturated polyester resins for composite applications. Two types of new unsaturated polyester resins were synthesized based on Bis-(2-hydroxyethyl) fumarate (I) and Bis-(6-hydroxyhexyl) fumarate (II). Bis-(2-hydroxyethyl) fumarate (I) and Bis-(6-hydroxyhexyl) fumarate (II) were synthesized from ethylene glycol and 1, 6-hexanediol with fumaric acid in the presence of p-toluene sulfonic acid as catalyst. The chemical structures were confirmed by CHN analyses, FT-IR and ¹H-NMR spectroscopy. New unsaturated polyesters were carried out by the condensation reaction between terephthaloyl chloride and the monomer I and II. The chemical structures of this polymer were confirmed by CHN analyses, FT-IR, ¹H-NMR, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). New oil palm empty fruit bunches (OPEFB) reinforced polyester composite derived from the new unsaturated polyester resins containing bis-(2-hydroxyethyl) fumarate and bis-(6-hydroxyhexyl) fumarate were prepared. The mechanical and physical properties such as tensile, flexural, impact properties and water absorption of OPEFB reinforced polyester composite were also studied. In general, the results showed that the new polyester reinforced OPEFB composite exhibits highest mechanical properties as compared to commercial polyester reinforced OPEFB composites.

CHAPTER ONE

INTRODUCTION

1.0 Introduction

For the past 20 years, advanced materials were characterized by a length development cycle. Today the use of composites materials in structures of all kinds was accelerating rapidly with the major impact already being felt in the aerospace industry where the use of composites has directly enhanced the capability of fuel-efficient in the commercial arena and new generation aircraft in the military sphere. A composite material is defined as solid materials, which consist of a combination of two or more materials in which the individual components retain their separate identities (Richardson, 1987; Marthur, 2006). In general composites were engineering materials combined to give permanence in service, which was superior to the properties of the individual materials (Hull & Clyne, 1996).

In recent years, owing to the increased environmental awareness, the usage of lignocellulosic fibers as a potential replacement for synthetic fibers such as carbon, aramid and glass fibers in composite materials have gained interest among researchers throughout the world. Extensive studies were done on lignocellulosic fibers such as sisal (Joseph *et al.*, 2002a & Jacob *et al.*, 2004), jute (Albuquerque *et al.*, 1999 & Mwaikambo & Ansell, 2002), pineapple (George *et al.*, 1995; Devi *et al.*, 1997; Mishra *et al.*, 2001 & Arib *et al.*, 2006), banana (Joseph *et al.*,

2002b & Adinugraha *et al.*, 2005) and oil palm empty fruit bunch fibers (Hill & Abdul Khalil, 2000; Rozman *et al.*, 2001; Khalil *et al.*, 2001) have showed that lignocellulosic fibers have the potential to be an effective reinforcement in thermoplastics and thermosetting materials.

According to Bledzki & Gassan (1999), Wambua *et al.* (2003) and Mishra *et al.* (2003), lignocellulose fibers offer several advantages over their synthetic fiber counterparts. Lignocellulose fibers were low cost raw material which was abundant in nature and renewable. Natural fibers can add to man-made fibers (glass, carbon, aramid fibers and etc) in the manufacture of high-matrix fiber composites. Natural fibers were cheaper than man-made fibers. According to Robson & Hague (1995), market pulp sell at £300/tonne, as compared to the price of glass fiber reinforcement was around £800-1,200/tonne. In fact, Zain (1994) had reported that, in Malaysia the cost of producing oil palm fibers was about £20/tonne. Natural fibers consume much less fossil-fuel derived energy in their production than do man-made fibers. It was estimated the energy content of fibers was as follows: carbon-130GJ/t, glass fibers-25GJ/t and natural fibers-5GJ/t (Bolton, 1994).

Owing to their low specific gravity, which was about 1.25-1.50 g/cm³ as compared to synthetic fibers, especially glass fibers, which were about 2.6 g /cm³, lignocellulose fibers were able to provide a high strength to weight ratio in plastic materials. The usage of lignocellulose fibers also provided a healthier working condition than the synthetic

fibers. This was due to the fact that, the glass fiber dust from the trimming and mounting of glass fiber components causes skin irritation and respiratory diseases among workers. For examples, there was some evidence of an 'asbestos type' condition arising from handling fiber (Cheremisinoff, 1990). Besides that, the less abrasive nature of the lignocellulose fibers offered a friendlier processing environment as the wear of tools was reduced. Furthermore, lignocellulose fibers offered good thermal and insulating properties, easily recyclable and were biodegradable especially when used as reinforcement in a biopolymer matrix.

These advantages have gained interest in the automotive industry where materials of lightweight, high strength to weight ratio and minimum environmental impact were required. Automotive giants such as Daimler Chrysler were using flax/sisal fiber mat embedded in an epoxy matrix for the door panels of the Mercedes Benz E-class model (Daimler Benz, 1996). Coconut fibers bonded with natural rubber latex were used for seat cushions in the Mercedes Benz A-Class model (Deem, 2003). Cambridge Industry, an automotive industry in Michigan, USA was making flax fiber reinforced polypropylene for Freightliner Century COE C-2 heavy trucks and also rear shelf trim panels of the 2000 model Chevrolet Impala (Sherma, 2003). Besides the automotive industry, lignocellulosic fiber composites such as jute fiber reinforced polyester have also found application in the building and construction industries such as panels, ceilings, and partition board (Roe & Ansell, 2002).

In recent years, thermosetting resins have received increasing attention from industry. Unsaturated polyester resins were frequently used as matrix materials in polymer composites such as fiber-reinforced plastic and polymer concretes. The polyester does not constitute the largest group among commercial synthetic polymers. Nevertheless, with respect to their range of application, they enjoy a leading position. First introduced as a material for synthetic fiber (Trevira) in 1953, poly(ethylene terephthalate) (PET) found new, interesting and enduring applications in many cases without any alternative. Unsaturated polyesters were broadly defined as condensation products of organic diacids and glycols. Unsaturation was incorporated in a variety of ways to produce terminal, pendant and internal double bonds. Of these types, internal unsaturation provided by maleic anhydride is most common.

Unsaturated polyester resins were widely used in a host of applications where advantage may be taken of their good range of mechanical properties, low cost, good corrosion resistance and low weight. Polyester resins were also used for clear casting, coatings, buttons, body fillers, work-surfaces (such as polyester marble), polyester concrete (for applications such as road drainage), cladding panels, sheeting, roofing tiles, pipes and also for application such as bathroom furniture (e.g. baths and shower trays).

However, unsaturated polyester resins products were still limited due to low chemical resistant as compared to expensive epoxy resin. This was because unsaturated polyester resins have low hydrolytic stability, and at the same time have low control over cure rate and reaction conditions than epoxy resins.

Therefore, by means of both chemical and physical modifications (new unsaturated polyester resin), it was possible to improve the end-use properties of the final products, but also find new applications. In this respect, the potential for recycling, based on the reactivity of polyesters was of particular importance. All these properties and information were very important knowledge about the possibility of using new polyester resin as a material in bio-composites paints and varnishes production, coating industry, etc.

1.1 Objectives of the Research

Many research before used natural fiber as fiber reinforcement and unsaturated polyester resin as matrix in composites. In Malaysia, natural fibers and unsaturated polyester resin were widely used as raw material in composites production. Previous studies were done (Alsina *et al.*, 2002; Khalil *et al.*, 2002 & Rozman *et al.*, 2002) by using conventional unsaturated polyester resin for composite application. Though in overseas, they had produced the new unsaturated polyester such as making polyester from stilbene derivatives (Young *et al.*, 1972),

synthesized polyester with mesogenic groups (Blumstein *et al.*, 1982) and making isophthalate polyester (Cusano *et al.*, 2000). In this research however new material like fumaric acid the *trans*-diacid was used as it is less corrosive and gives lighter-colored products with slightly improved heat resistance and the simplest diol, ethylene glycol, gives polyester with a tendency to crystallize. The main objectives of this research were summarized below:

- 1) To synthesize and characterize the structures of new unsaturated polyester resins.
- 2) To study the influence of methylene spacers of the new unsaturated polyester resins on thermal and mechanical properties.
- 3) To investigate the physical and mechanical properties of the new unsaturated polyester reinforced composites.

CHAPTER TWO

LITERATURE REVIEW

2.0 Composite Materials

According to ASTM International Handbook Committee, 1973, composite material was defined as a macroscopic combination of two or more distinct materials, having a recognized interface between them. However, because composites were usually used for their structural properties, the definition were restricted to include only those materials that contain reinforcement (such as fibers or particles) supported by a binder (matrix) material. Composite material is also defined as a heterogeneous mixture of two or more heterogeneous phases which were bonded together (Kelly, 1994).

The earliest example of a composite material were traced back in the third millennium BC when Egyptians made bricks from clay reinforced with straw (Matthews & Rawling, 1999).The Mongolians though produced bows which were made from a combination of wood, animal tendons and silk. As early as 1908, the first composite materials were applied for the fabrication of large quantities of sheets, tubes and pipes for electronic purposes. In 1986 for example, aeroplane seats and fuel-tanks were made of natural fibers with a small content of polymeric binders. Today, a renaissance in the use of composite material in technical applications was taking placed in the automobile and packaging industries (Bledzki & Gassan, 1999).

Composite materials were divided into natural occurring composite and synthetic composites. Many natural occurring materials were classified as composite materials. Examples of natural composites were wood which was made up of cellulose molecules in a lignin matrix, teeth and bone which were composed of hydroxyapatite in a matrix of collagen, insect exoskeleton and to name a few. Synthetic composites were concrete which a combination of stone and cement, asphalt and also fiberglass which was a glass fiber reinforced unsaturated polyester matrix.

2.0.1 Definition of Composite

Nowadays composite materials have recently gained much attention due to their superior properties and wide variety of applications. Composites also one of the fastest growing industries and continue to demonstrate a marked impact to the materials world. Composite can have many meanings and arbitrary classifications (Askeland, 1988; Schwartz, 1992). There appeared to be no completely acceptable universal definition for a composite material. The Oxford dictionary for example, defined a composite as something made up of distinct parts (or constituents). In the broadest definition, any product composed of two or more materials whether metallic, organic, or inorganic and having recognizable interface between them was a composite (Schwartz, 1992; Reinhart & Clement, 1987). According to Jordan (2002), the noun composite was derived from the Latin verb *componere* which mean to put together. Therefore composite materials were considered as a material which was formed when two or more chemically distinct constituents are combined together on a macro scale (Schwartz, 1992).

Schwartz (1992) further stressed that the constituents in a composite material were physically identified and exhibit an interface between one another. A more detail description of a composite material was given by Agarwal & Broutman (1990) who defined a composite as a material that consisted of one or more discontinuous phases which were usually hard and strong embedded in a continuous phase. The continuous phase was called the matrix while the discontinuous phase was termed the reinforcement material. According to Hepler (1963), composite material consisted of three basic elements: fiber, matrix and the fiber-matrix interface. Each of these elements must have appropriate characteristics and function both individually and collectively in order for the composite to attain the desired superior properties. Meanwhile, Milewski & Katz (1987) described composite as materials that contain a strong, stiff fiber reinforcing material supported by a more flexible binder or matrix material.

2.0.2 Classifications of Composite Materials

Based on the definition of a composite material, composites were produced by any combination of two or more materials which can be metallic, organic or inorganic. Each of these elements must have appropriate characteristics and function both individually and collectively in order for the composites to attain the desired superior properties. The fiber contributed the high strength and modulus to the composite. It was the element that provides resistance to breaking and bending under applied load. The main roles of the matrix were to transmit and distribute stresses among the individual fibers, and

to maintain the fibers separated and in the desired orientation. The matrix also provided protection against both fiber abrasion and fiber exposure to moisture or other environmental conditions, and caused the fibers to act as a team in resisting failure or deformation under load. The maximum service of the composites was limited by the matrix. Other desirable features of the matrix were resistance to liquid penetration and freedom from voids (Milewski & Katz, 1987). Schwartz (1992) cited that the most widely used constituent forms in a composite material were fibers, particles, laminae or layers, flakes, fillers and matrixes.

Composites were divided into classes in various manners. One simple classification scheme was to separate them according to the morphology of reinforcement and also on the matrix material. Classifications of composite materials according to the reinforcement forms were particulate reinforced composites, fiber reinforced composites and structural composites. Particles by definition were non-fibrous in nature and have roughly equal dimensions. Spherical, cubical, tetragonal, platelet or other regular or irregular shapes were the common shapes of particles used as reinforcements in composites. (Agarwal & Broutman, 1990).

According to Schwartz (1992), fiber reinforced composite materials consisted of fibers of high strength and modulus embedded in or bonded to a matrix with distinct interfaces between them. Fiber reinforced composites were composed of reinforcing fibers which were characterized as a long fine filament with an aspect ratio of greater than 10 (Hepler, 1963). Glass, carbon,

aramid, boron and cellulose fibers were widely used as reinforcement in composite materials. Structural composites though, consist of laminate and sandwich composites, which were used in structural engineering applications.

In addition, the major classes of structural composites that exist today were categorized as polymer matrix composites (PMCs), metal matrix composites (MMCs), ceramic matrix composites (CMCs), carbon-carbon composites (CCCs), intermetallic composites (IMCs), or hybrid composites (HCMs) (Hull & Clyne, 1996; Schwartz, 1992; Reinhart & Clement, 1987). According to Hull & Clyne (1996) most composites in industrial use were based on polymeric matrices. However, the primary drawback to PMCs was the low maximum temperature at which they used. Higher temperatures call for MMCs or CMCs. Metal matrix composites were primarily employed because they were more fracture tough than the matrix on which they were based. Polymer matrix composites (PMCs) were relatively inexpensive owing to their low setting and forming temperatures (Courtney, 1990). However, the focus of this research was mainly on polymer matrix composite.

2.0.3 Fiber Reinforced Composites

Fiber reinforced composite materials were especially useful composites because they contained a reinforcing phase in which high tensile strengths were realized when they were processed to fine filaments, wires or fibers. In such fiber composites, the matrix “glues” the fibers together and also transferred stress to them. In many cases, the matrix also protected the fiber from deleterious interactions with the environment, such as oxidation or corrosion.

Thus, many fiber-reinforced materials consisted of a high-strength material imbedded in a much less strong matrix (Courtney, 1990).

Fiber reinforced composites materials offered a combination of strength and modulus that was either comparable to or better than that of traditional metallic materials. Because of their low specific gravities, the strength-to-weight ratios and modulus-to-weight ratios of these composite materials were markedly superior to those metallic materials. In addition, fatigue strength-to-weight ratios, as well as fatigue damage tolerances, of many composite laminates were excellent (Shackelford, 2000).

Fiber reinforced composites or commonly known as FR were now competing with traditional materials such as steel, wood, aluminum, and concrete in various engineering applications. Fiber reinforced plastics composites have found applications in automobiles, boats, aircrafts and as construction materials. This was because unlike the conventional materials mentioned above, fiber reinforced plastic composites have excellent specific mechanical properties (high strength to weight ratio), corrosion resistance and are low cost. The properties of a fiber reinforced plastic composites were mainly governed by the fiber, matrix and interface. Thus, the following chapters deal in detail with the functions and characteristics of these components (Courtney, 1990).

2.0.4 How does a composite work?

In this research, composite was composed of two main components; the fiber as reinforcement and the matrix. The reinforcing element was able to sustain high tensile loads whilst the matrix imparts rigidity to the composite. The application of stress to the composite results in transfer of loads from one fibre to another, via the matrix. The stiffness of the matrix was often accompanied by brittleness. However, the combination of fibre and matrix made for a tough material.

In general, composites may fail by one or two mechanisms, plastic flow or brittle cracking. The material defined the mechanism; metals (which were ductile or tough) generally yield before they crack, while non-metallic materials (apart from some polymers) crack before they yield and are therefore brittle. Fibre composites failed from defects in the material. These were broken fibres, flaws in the matrix or debonded from the matrix. This separation of the interface used energy of the stressed system. When total separation occurred at the fibre-matrix interface, the strain energy of the debonded length of the failure was lost as heat. The separated fibre were pulled out from the matrix and energy was then lost from the system in the form of frictional energy. The fibre was then left intact as the crack propagates. Sufficient stress, if transferred to a fibre will however, caused the fibre fracture. It was explained by the Cook-Gordon theory (Shackelford, 2000).

2.1 Matrix Materials

In general, matrix materials cover the range from polymers to metal to ceramics. The matrix was a substance that was capable of holding the reinforcing materials together by surface attachment. Matrix is also defined as material that gives body and grips or holds the reinforcement of the composite together, and was usually of lower strength than the reinforcement. The purpose of the matrix in composite was to bind the fibers together by virtue of its cohesive and adhesive characteristics, to transfer load to and between fibers, and to protect them from environments and handling (Reinhart & Clement, 1987). The matrix also served as a binder which holds the reinforcing materials in its place. Besides that, when a composite was subjected to an applied load, the matrix deformed and transferred the external load uniformly to the fibers. The matrix also provided resistance to crack propagation and damage tolerance owing to the plastic flow at crack tips (Shwartz, 1992).

Furthermore, the matrix also functioned to protect the surface of fibers from adverse environmental effects and abrasion especially during composite processing. Matrix also kept the reinforcing fibers in the proper orientation and position so that they were carried the intended loads, distributed the loads more or less evenly among the fibers, provided resistance to crack propagation and damage, and provided all of the interlaminar shear strength of the composite. Furthermore, the matrix generally determined the overall service temperature limitations of the composite, and also control its environmental resistance (Reinhart & Clement, 1987).

Matrix was used to embed such strong fibers was required to provide a strong and stiff solid for engineering purposes. The properties of the matrix were usually chosen as complementary to the properties of the fibers; for example great toughness in a matrix complements the tensile strength of the fibers. The resulting combination were then achieved high strength and stiffness due to the fibers and resistance to crack propagation. It was also due to interaction between fibers and matrix. Matrices were generally be classified into two major types which were thermoplastics and thermosets. The selection criteria of the matrices depend solely on the composite end use requirements. For example, if chemical resistance together with elevated temperature resistance was needed for a composite material then thermoset matrices were preferred than thermoplastics. Whereas, if a composite material with high damage tolerance and recyclables was needed then thermoplastics were preferred (Shackelford, 2000).

2.1.1 Thermoset

Thermoset resin was defined as a plastic material which was initially a liquid monomer or oligomers or a pre-polymer, which was cured by either application of heat or catalyst to become an infusible and insoluble material. Thermoset polymers have covalent bonds linking the polymer chains in three dimensions. These links prevent the chains from sliding past one another resulting in a higher modulus and improved creep resistance. Usually thermosets were more brittle than thermoplastics. The polymer chains in thermosets were below their glass transition at room temperature, making them glassy.

Prior to cure, thermosets were liquid or made to flow under pressure to any desired form. Once cured, a tightly bound three dimensional network structure was formed in the resin and hence the resin cannot be melted, reshaped and reprocess by heating (Matthews *et al.*, 1999; Hull *et al.*, 1996). Therefore, during composite manufacturing, the impregnation process followed by the shaping and solidification were done before the resin begin to cure (Courtney, 1990). However according to Shackelford (2000), thermosetting products were removed from the mold at the fabrication temperature, typically 200 to 300°C.

Thermoset resins were brittle at room temperature and have low fracture toughness. On the other hand, owing to its three dimensional cross linked structure, thermoset resins have high thermal stability, chemical resistance, high dimensional stability and also high creep properties (Matthews & Rawling, 1999; Shwartz, 1992). Thermosetting polymers also offered high electrical and thermal insulating properties that important in electrical industries (Courtney, 1990). However, thermosets have the disadvantages of not being recyclable and, in general, having less variable processing techniques (Shackelford, 2000).

Among the most common thermosetting resins used in composite manufacturing were unsaturated polyesters, epoxies, vinyl esters, amino resin and phenolics. In this research, unsaturated polyester resin was preferred due to their good range of mechanical properties, relatively low cost, corrosion resistance and low molecular weight. Therefore, polyesters were suitable for a

variety of applications and are adaptable to the fabrication of large structures (Matthews & Rawling, 1999; Hull & Clyne, 1996; Shwartz, 1992).

2.1.1.1 Current Interest Research of Unsaturated Polyester

Polyesters were important class of high performance and engineering polymers, which find use in a number of diverse applications (Lorenzetti *et al.*, 2005; Tiitu *et al.*, 2005; Qazvini & Mohammadi, 2005). Unsaturated polyester resin were chosen first for making fibre reinforced plastics (FRP) by any molder because of the ease of handling and fabrication and the low cost as compared to epoxy resin. They were primarily used in compression molding (sheet molding compounds), injection molding (bulk molding compounds), resin transfer molding, pultrusion, filament winding and hand lay-up process (Vilas *et al.*, 2001). About 85% of the FRP products like boats, car and aircraft components and chairs) were manufactures using polyesters (Devi *et al.*, 1997).

Different kinds of polyesters were synthesized over the past decades from various types of diacid chlorides and diols. Thermally stable polyesters derived from isophtalic and terephthalic acids with bisphenol-A was commercialized (Cavallo *et al.*, 2005). However, polyesters were generally difficult to process because of their limited solubility in organic solvents and their melting temperature or high glass-transition temperature by virtue of their rigid structures (Tamami *et al.*, 2004). Therefore development of polyesters for use at high temperature with improved solubility was an important goal.

One of the approaches to improved solubility as well as processability of the polymers without extremes loss of their high thermal stability was the introduction of polar and flexible groups into the polymer backbone (Messori *et al.*, 2001; Ito *et al.*, 2001; He *et al.*, 2001; Martin, 1999; Huang & Jiang, 1998). The incorporation of bulky pendent groups were also provided beneficial effect for solubility because this approach produces a separation of chains and lowering the chain packing with a molecular mobility, so that the overall observable effect improvement of solubility at the same time (Cook *et al.*, 1998; Li *et al.*, 1998; Klein *et al.*, 1998; Lange *et al.*, 1997; Grobelny, 1997). It was well known that a large number of polymers containing heterocyclic ring in the main chain were resistant to high temperature (Blumstein *et al.*, 1982).

Recently, the researchers synthesized new polyesters containing rigid segment such as pyridine rings that possess high glass transition temperatures and enhanced solubility in organic solvents (Lee *et al.*, 2005; Wu *et al.*, 2005). Current interest in unsaturated polyester (UP) resins also focused on the enhancement of chemical inertness, solvent and high temperature resistant, barrier properties, low friction coefficient and low surface tension, that in principle were transferred to other polymeric materials by blending or copolymerization. Some enhancement such as excellent resistance to corrosion, water and atmospheric agents, formulations for resins and foams and several others were also reported in patent literature (Messori *et al.*, 2001).

Nowadays, the macroscopic properties of polymers and other complex materials were mainly interpreted based on understanding the underlying microscopic phenomena. Particularly, appreciating the temperature dependence of the average relaxation time may be end up designing molecular mobility and lead to fine tuning the final properties. Toward this end, Angel had developed an energy landscape model based on the nature of structural evolution in a super cooled liquid approaching the glassy state. According to this scheme, relaxation behavior were considered as strong and fragile, depending on the rate with which the associated properties were modified as the temperature passes through the glass transition region (Qazvini & Mohammadi, 2005).

The continuing search for polymers with improved or unusual properties had lead to a considerable level of interest in the behaviour of so called rigid rod polymers. Such materials were of interest because of their potential to form fibers of particularly high strength (Lorenzetti *et al.*, 2005; Tiitu *et al.*, 2005; Qazvini *et al.*, 2005). This rigid-rod polymer had achieved commercial success in a variety of applications, especially those which rely on its unique combination of high-strength and low density (Messori *et al.*, 2001). The major drawback to the commercial exploitation of the many rigid-rod systems was their lack of processibility. However, the usage of unsaturated polyester resin had used to enhance the drawback (He *et al.*, 2001).

Unsaturated copolyesters, also called polyester resins, were based on macromolecules with a polyester backbone in which both a saturated acid and unsaturated acid were condensed with a dihydric alcohol (Qazvini & Mohammadi, 2005). A survey of the scientific literature reveals that few unsaturated copolyesters based on the interaction of unsaturated diols and saturated acids were synthesized and studied (Cavallo *et al.*, 2005; Tiitu *et al.*, 2005). Imai and Tassavori synthesized and studied aromatic polyesters and copolyesters containing phenylindane units with T_g 235- 253°C (Messori *et al.*, 2001).

In recent years much emphasis had been given to the synthesis of polymers containing chromophoric groups. For example, the aromatic azo groups which can form a part of the main chain (Ito *et al.*, 2001). The aromatic azo group was of special interest because of the existence of cis-trans isomerism and its effect on the photochromic properties of the polymers. Therefore, polymers that contained the azo group have potential use in a variety of applications (Cook *et al.*, 1998; Klein *et al.*, 1998; Li *et al.*, 1998). The present investigation deals with the synthesis and characterization of new unsaturated polyesters and co-polyesters based on some dibenzylidenecycloalkanones and containing meta- and para-azo groups in the main chain. A major purpose of this work was to investigate the effect of a cycloalkanone ring, in the polymer backbone, on polymer properties. Moreover, the crystallinity, thermal stability, and electrical properties of the synthesized polyesters and copolyesters were examined and discussed. New interesting classes of linear unsaturated

polyesters based on dibenzylidenecycloalkanones were synthesized by interfacial polycondensation of various monomers (Gomez *et al.*, 2006).

2.1.1.2 Classification

Polyesters were broadly classified into unsaturated and saturated polymers. These were two broad divisions subdivided as follows: (Bruins, 1976)

1. Unsaturated

a) Laminating and Casting Resins. These were based on dibasic acids and dihydric alcohols. The polyester unit formed must be capable of copolymerizing with a vinyl-type monomer, thereby yielding a vinyl-polyester copolymer or simply cured polyester having a thermoset structure.

b) Alkyds. In general, the same types as (a) although the glyptal (surface coatings) types are modified with oils or fatty acids. This term was also used to describe a group of thermosetting moulding materials based on the reaction of a dihydric alcohol with an unsaturated acid such as maleic in place of the conventional phthalic acid. A vinyl type monomer was also necessary to affect speedy cross-linking and curing and used as moulding powders for compression and transfer-moulding techniques.

2. Saturated

a) Fibres and Films. These were based on the reaction of terephthalic acid with ethylene glycol and were linear, high molecular weight polymers which do not undergo any cross-linking reactions.

b) Plasticizers. These were polyesters which were completely saturated, normally referred to as polymeric plasticizers.

c) Polyester/ Polyurethanes. Certain polyesters having high hydroxyl content were reacted with various isocyanates to form polyurethanes, which were finding extensive use as foams, elastomers, surface coatings and adhesives.

However, in the present study, unsaturated polyester resin was used.

2.1.1.3 Preparation

Polyesters were polymers with repeating carboxylate groups in their backbone chain. The polyester backbone was generally composed of three basic types of structural units, saturated acids, unsaturated acids and glycols (Figure 2.1).

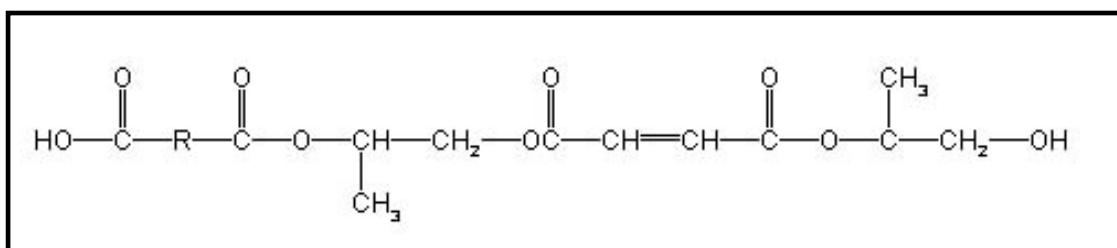


Figure 2.1: Anhydrides Acid, Acids, Unsaturated Anhydrides Acids and Alcohols Formed Polyester. Brydson, (1989)

In the case of the general-purpose polyester, these components usually consisted of phthalic acid, maleic acid, and propylene glycol. This was a very desirable composition since it had the characteristics of low cost and good quality; propylene glycol and phthalic anhydride were the lowest cost raw

material in their class. The unsaturated acid provided the sites for cross-linking, the saturated acid determined the degree of spacing and the glycol, of course, provided the means for esterification and for bridging the acids to form a polymer. Linear unsaturated polyesters were prepared batch wise by heating and cooling and fitted for distillation. A typical formulation for a general-purpose material were as follows; propylene glycol, 100 parts by weight, maleic anhydride, 72 parts by weight and phthalic anhydride 54 parts by weight. Typical reaction conditions were 150-200 °C for 6-16 hours, and hydroquinone was commonly used as the inhibitor. The conversion of the reaction was 90-95%. The unsaturated polyester resins were also prepared by the reaction of diphenol or diol with an aliphatic diacid chloride (Boenig, 1964).

First produced commercially in the late 1920s, polyesters have become important compounds used in a wide variety of industries. The most economically important types of polyesters include poly (ethylene terephthalate) (PET) and poly (butylene terephthalate) (PBT). The chemical reactions for making polyesters were investigated in 1901 and resulted in the production of glyptal polyesters. These reactions involved the combination of a diacid with a diol. The reaction was called a condensation reaction because the two initial types of monomers combined to produce a longer chain polymer and water as a by product.

Linear polyesters were not produced until the 1930s, when W. H. Carothers systemically investigated reactions of diols with diacids. Carothers was not successful in producing a polyester fiber and switched the focus of his

research. In 1942, John Whinfield and W. Dickson made the first high molecular weight PET. After these fibers were produced other polyesters were discovered and have since become very important compounds (Sandler, 1974).

Linear unsaturated polyesters were prepared commercially by the reaction of a saturated diol with a mixture of an unsaturated dibasic acid and a modifying dibasic acid. In principle, unsaturation desired in a polyester can be derived from either an unsaturated diol or an unsaturated acid provides sites for subsequent cross-linking; the function of the modifying acid was to reduce the number of reactive unsaturated sites along the polymer and hence to reduce the cross-link intensity and brittleness of the final product. Some acids and anhydrides which were used to modify polyester are, in fact, unsaturated but the double bonds were not sufficiently reactive to represent sites for subsequent cross-linking (Saunders, 1988).

Unsaturated polyester resins were addition products of various saturated acids, unsaturated acids and glycols. Many patents for the preparation of these products were issued within the past 30 years. The polymers making up this first group of polyesters were linear polyesters containing aliphatic unsaturation which provided sites for subsequent cross-linking. A polymer of this type first became available in the U.S.A in 1946; the polymer was prepared from diethylene glycol and maleic anhydride and could be crosslinked by reaction with styrene (Saunders, 1988).