CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

Human development is clearly linked to continuous improvements in the use of materials. Amongst the materials, polymers are widely used for technical purposes; indeed, polymers are major industrial materials used in the building, construction, packaging, transportation, electronic as they exhibit some specific properties such as thermal stability, electrical insulation, flexibility, resistance to chemicals and adhesion to metallic substances.

Polymer materials find important application in paints and coatings industry. They are used for corrosion control, providing chemical and heat resistance to the coated substrates as well as decoration. Special coating can provide camouflage in military application, anti-fouling and anti-bacterial protection, and for many other reasons. The terms paint and coating sometimes are used interchangeably, but there are differences in their meanings. Coatings generally refer to materials used for protective and functional purposes, while paints refer to materials used for decorative purposes. However, there exist many similarities in handling, composition, and the use of paints and coatings. The four main components of a coating are:

Resin: The binder that holds the pigment particles together and supplies adhesion of the coating to the substrate. Most coatings are named by the generic composition type of resin used, i.e. phenolic, epoxy, polyurethane, acrylic, polyester, alkyd and etc. Resin is responsible for most of a coating's chemical and physical properties, including abrasion, hardness, weather resistance, chemical resistances, cohesion and adhesion. The type of resin determines the coating’s curing mechanism as well.

Pigment: Generally, the primary purpose of pigment is to provide colour and opacity to the coating film and may also supply weathering, durability, and protection to the light-sensitive resins. Extenders or filler pigments add mechanical strength to the coating film, reduce settling, control viscosity, improve film build and control gloss. While, there are many important types of coatings containing little or no pigment and these are known as the clear coatings.

Solvent: The main function of the solvent is to provide ease of coating application. Solvents provide flow-out, control adhesion, leveling during application and durability of the film.

Additives: Additives are small amounts (usually less than 3%) of special materials that could impart specific properties to the coating. The type of additives changes widely depending on the resin type. For examples, plasticizers function to produce flexible films, driers in alkyd-based coatings to accelerate the film forming process, wetting agents to improve the spreading. Besides, dispersants, film-forming aids and anti-microbial agents, are some other examples of additives that may be incorporated into a coating formulation to suit different requirements.

The paint and coatings industry could be divided into three market categories: (1) architectural (decorative) coatings; (2) industrial coatings; and (3) specialty coatings. The architectural category includes lacquers, varnishes, and all paints sold for direct application to either exterior or interior surfaces of residential, commercial, institutional, and industrial buildings. These include house paint, satins, and undercoats. Figure 1.1 shows consumption of paint and coatings by country and market. According to this figure the largest proportion of paint used is accounted for architectural coatings.

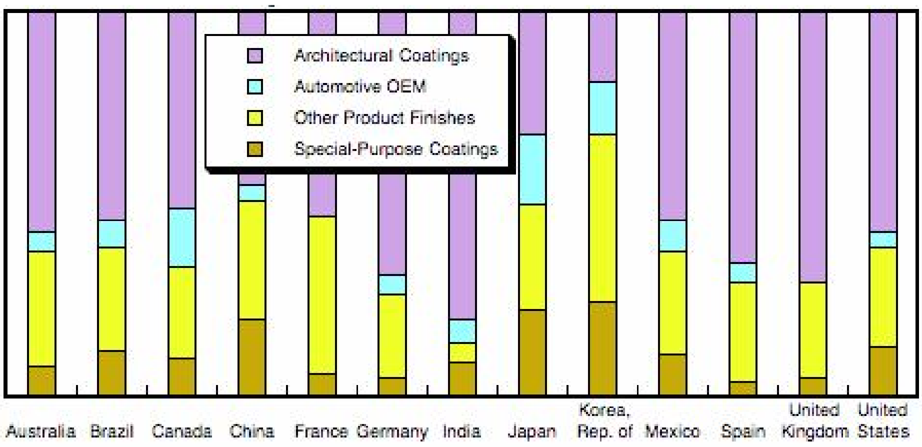


Figure 1.1 : Analysis of paint consumption by market in 2007 (Source: Paint and Coatings Industry Overview 2009)

Most commercial polymers are derived from petroleum feedstocks. Therefore, as the number of applications of polymeric materials continue to increase, an alternative source of these materials becomes more important. Prior to the discovery of petroleum, natural fats and oils were frequently used as a source of energy, light and raw materials. With the first drilling of petroleum wells, sometime in the middle of the nineteen century, these natural fats and oils began to be replaced slowly by petroleum by-products.

Using natural fats and oils to replace some of the petroleum-based chemicals for polymer production is becoming attractive because they are sustainable resources and more environmental friendly. The most notable benefit is that these oils are rapidly renewable. Whereas, it takes millions of years for new petroleum reserves to form, while oil-bearing plants are easily replenished annually. From an environmental viewpoint, natural fats and oils are much safer to transport than petroleum. Additionally, there is an abundance of world oilseed production and also Malaysia is one of the largest important producers of palm oil. The production of natural oils is controllable via emerging genetic engineering tools [1-4]. This allows controlling the amount of oil produced by plants as well as the molecular structures. Therefore, natural oils are considered to be the most important class of renewable sources.

As with alkyd resin, it was one of the first applications of synthetic polymers in surface coatings technology; it was a successful process in chemically combining oil or oil-derived fatty acids into a polyester structure. The major reaction in alkyd preparation is the esterification reaction between alcohol and acid. By the early 1950s, alkyds had become the preeminent binder for coatings. Alkyd consumption in the USA reached a plateau at about 3×10^5 t/a in 1960-1980 and then began declining at a rate of about 2%/a, reaching about 2.3×10^5 t/a in 1996 [4]. Rising petrochemical prices have increased interest in all polymers made partly from renewable and environmental friendly resources. Alkyd resins have obtained a good reputation because of their economy and ease of application. Additionally, these materials are to greater extent biodegradable polymers because of the glycerol and oil parts.

Another category of coating material is the acrylic resins. Acrylic polymers are widely used for their excellent properties of transparency, strength, chemical and weather resistance. The term acrylic has been used to describe those polymers containing acrylate and methacrylate esters in their structure along with certain other vinyl unsaturated compounds. Acrylics are employed as general-purpose coatings, anticorrosive coatings for metals, wire enamel and so on; these are commonly one-component low-viscosity solution coatings, formulated either as spray or dip types and as either air-drying or baking types. Various references in the literature fully discuss the formulation and use of acrylic polymers in coatings [5,6].

Acrylic enamels are thermally very stable and retain their initial clarity and color characteristics at temperatures as high as 260°C. For electrical insulating applications, maximum continuous operating temperatures depend on the formulation and may range from 95 to 155°C. The electrical properties of acrylics are, in general, very stable at room temperatures. However, they are not as good as those of epoxies or silicones, which are stable over a wider temperature range.

1.2 Types of coatings

There are many types of coatings in the market. Coatings can be classified into many different types depends on composition or solvent. However, most commonly used coatings are conventional high solid coatings (solvent borne), water-borne coatings and powder coatings. These types of principal categories of coatings are described in the next section.

1.2.1 High-solid coatings (Solvent borne)

Historically majority of coatings were solvent borne. The need to minimize volatile organic compounds (VOC) emissions had resulted in attempts to increase solids content of coatings. One of the important approaches has been to decrease the solvent content of solvent-borne coatings by formulating so-called high solid coatings. Production of high-quality organic coatings with low solvent amount is an important target in coating industry. Decreasing the viscosity of the polymer reduces the amount of organic solvent. Preparation of a low viscosity coating requires the use of polymers having either a low molecular weight or a narrow molecular weight distribution. For this target, many investigators suggested different methods for preparation of low viscosity resins [6-8].

Reducing the use of organic solvent can be achieved by synthesizing resins having a highly branched structure. For this purpose, star and hyper branched structure resins were prepared by Manczyk K, Szewczyk P [9]. The resulting resins were tested in the form of varnishes and white enamels. The high functionality obtained using tripentaerythritol also gives alkyds that crosslink as rapidly as shorter oil length, higher viscosity alkyds [10, 11].

Dendritic polymers are also a class of polymers characterized by a impenetrably branched backbone and a large number of reactive groups. The low viscosity infers that dendritic macromolecules are less entangled due to their spherical shape; they have lower intrinsic viscosities than their linear shapes. This is due to their highly branched, dense and globular non-entangled structures; their viscosity decreases with the addition of the solvent and they are more soluble than the linear polymers. Ceylan Karakaya et al. synthesized hyperbranched resins containing fatty acids. Dipentaerythritol which has six hydroxyl groups was used as a core molecule and it was transesterified with castor oil. It was concluded that the use of highly branched resins reduced the need for solvent [12].

Some increase in solid can be achieved by change of solvent. Aliphatic (and to a somewhat lesser degree, aromatic) hydrocarbon solvents promote intermolecular hydrogen bonding, especially between carboxylic acids, also between hydroxyl groups, thereby increasing viscosity. Use of some hydrogen-bond acceptor solvent, such as ester or ketone or hydrogen-bond acceptor-donor solvent such as an alcohol, gives a significant reduction in viscosity, so that resin solutions of lower viscosity can be obtained with less solvent.

Another method to high solid alkyd coatings is to use reactive diluents in place of portion of the solvent. The opinion is to have a component of lower molecular weight and much lower viscosity than alkyd resin, which reacts with the alkyd during drying, and so it is not part of the VOC emissions. The use of reactive diluents is reviewed by K. H. Zable [13]. Several other types of reactive diluents have been used to formulate high solids alkyd coatings. Polyfunctional acrylate monomer such as trimethylolpropan trimethacrylate have been used in force dry coatings (coatings designed to be cured in the range of temperature between 60-80˚C [14]. D. B. Larson and W. D. Emmons used dicyclopentadienyloxyethyl methacrylate as a reactive diluent [15]. It is difunctional because of the easily abstracable allylic hydrogen on the dicyclopentadiene ring structure and methacrylate double bond.

1.2.2 Water borne coatings

Increasingly due to ecological reasons, solvent-based industrial paints are being replaced by water borne products. Water borne coatings, which currently account for about 51% of the total volume of coatings produced in the United States, are projected to grow at an annual rate of between 5 and 7% through 1999 [16].

Coatings that utilize water as the major carrier liquid have been described by a variety of different terms, including water borne, water reducible, water soluble, emulsions and latex. By definition, water borne generally defines the broad category of coatings that utilize water as the main volatile liquid component. Each of the other terms listed above have a specific meaning in relation to water borne coatings. The term water reducible describes specific water borne coatings whose viscosity can be easily reduced upon the addition of more water. A water soluble coating formulation refers to the ability of water to dissolve the binder forming a true solution. Finally, the term emulsion refers to a dispersion of liquid (i.e. polymer) droplets in water medium. Latex paint can be made through the use of emulsion polymerization; the resulting paint contains a dispersion of polymerized resin particles [17].

The resins commonly used in conventional solvent borne coatings are usually modified by increasing their hydrophilic nature prior to being incorporated into a water borne coating formulation [18]. Typical resin chemistries include acrylics, alkyds, polyesters, epoxies, polyurethanes and vinyls [19, 20] with common crosslinkers being melamines, aziridines, carbodiimide and glycidyl compounds [20]. The acrylic resin compounds are used in a variety of industrial applications and in the automotive industry

[21]. Acrylic latexes based on multiphase particles are currently under development. Research and development efforts in water borne coatings have been directed towards stabilizing against changes that occur from temperature, improving overall performance and reducing co-solvents that are required [22]. The emulsions are stabilized with surfactants and can be prepared with little, if any, volatile solvent. Co-solvents, which may comprise up to 30% of the total liquid present in a water borne formulation, are commonly used to provide adequate flow, film formation, wetting and drying [18]. The incorporation of polar functional groups, such as carboxylic acid, sulfonic acid and tertiary amine groups in a polymeric surfactant helps both water solubility and dispersibility of water insoluble polymers [22]. There are limitations in use of alkyd coating emulsions [23]. It was observed that the surfactant tends to bloom to the surface of the films formed from emulsions of long alkyds, leaving pits in the dry film. It is common to add a few percent of an alkyd-surfactant blend to latex paints to improve adhesion to chalky surfaces and in some cases to improve adhesion to metals. Hybrid alkyd-acrylic has been produced by dissolving an oxidizing alkyd in the monomers used in emulsion polymerization, yielding latex with an alkyd grafted on the acrylic polymer [24, 25].

Another method is to make alkyds with an acid number in the range of 50, using secondary alcohols or ether alcohols as solvents. The acid groups are neutralized with ammonia or an amine. The resultant solution can be diluted with water to form a dispersion of solvent swollen aggregates in water. Molecular weight can be higher than solid alkyd. Use of the primary alcohol solvents should be avoided because they can more readily transesterify with the alkyd during resin production and storage, leading to reduction in molecular weight [26].

After the film is applied, solvent and amine evaporate, and the film crosslinks by autoxidation. Since there are a fairly large number of residual carboxylic acid groups left in the crosslinked binder, the water resistance and particularly the alkali resistance of the films are reduced, but are still satisfactory for some application [27]. Hydrolytic stability can be a problem with water-reducible alkyds. Acrylated fatty acids can be used to synthesize water-reducible alkyds with improved hydrolytic stability.

In water borne coatings, the major problem arises from the unique evaporation characteristics of water. The vaporization heat and heat capacity of water are high, resulting in high energy requirements for evaporation. Water evaporates more slowly than solvents with similar vapour pressures. However, the vapour pressure increases rapidly with increasing temperature. On the other side, the evaporation of water is affected by relative humidity and can lead to serious problems. The higher surface tension of water compared to organic solvents can be decreased by using surfactants in latex paints. However, the presence of surfactants causes to give films with poor water resistance. In the case of water reducible coatings, before addition of water, pigments can be dispersed in solvent solutions of the resins and the surface tension can be decreased by the use some organic solvent such as butyl alcohol or propylene glycol or a butyl ether of ethylene in the formulation [28].

1.2.3 Powder coatings

Powder coating is a part of industrial coatings that is being developed during this decade because of environmental concern. This type of coatings is used as a dry powder and does not require a solvent to keep the binder and fillers in a liquid suspension form. The powder coating process involves application of dry finely ground particles of pigment and resin to surfaces prior to a curing process. The coating is typically applied electrostatically, and then cured under heat to allow for flow and coating formation.

Resins used in powder coatings are of two categories thermoplastic and thermosetting. The binders for thermosetting powder coatings are made up of a mixture of a primary resin and a cross-linker. Baking the thermosetting powder causes a reaction with other chemical groups in the powder to give the polymer strength, resulting in a high molecular weight product. The main resin types used in thermosetting powder coatings are all familiar to the liquid coatings chemist. The most common binders used are acrylic, polyester, and epoxy that they are well known in liquid coatings. However, curing agents and the molecular weight are slightly different. There are five types of powder coating systems that are derived from these three general resins: epoxy-polyester, epoxy, polyester-TGIC (Triglycidyl isocyanurate), polyester-urethane and acrylic-urethane [29, 30]. Nylon, Polypropylene, vinyl, polyvinyl chloride, polyethylene and polyvinylidene fluoride are used as binder for thermoplastic powders. The thermoplastic powders do not undergo any additional reactions during the baking process, but rather flows out into the final coating. Properties and application procedures of these two types of powder differ significantly [31].

There are several advantages for powder coatings over conventional liquid coatings: i) Environmental friendliness-no solvents are required and emit near zero VOC. ii) Powder coatings can produce much thicker coatings than conventional liquid coatings. iii) Its overspray can be recycled and thus it is possible to achieve nearly 100% use of the coating. iv) The cost of equipment and operating for a powder line are generally cheaper than for conventional liquid lines. v) Finishes are tough and flexible making, it harder to chip or crack. However there are some short comings for this kind of coating: for example very thin coatings can show pinholes. Also, colour matching and uniformity can be harder than with liquid paints. This kind of coating is limited to spray and fluidized bed methods [31]. In addition because of high baking temperature, only substrates that can withstand the baking cycle can be used. This limits its applications to metal substrates.

1.3 Chemistry of alkyd resins

Alkyds are prepared by condensation polymerization of polyhydroxy alcohols, polybasic acids and fatty acids. They are polyesters, but in the coatings field the term polyester is reserved for “oil-free polyesters”. Coatings from vegetable oils have been used for at least 600 years. The terms “alkyd” was first proposed by Kienle in 1927 and was coined from the “al” of alcohol and the “kyd” represents the last syllable of acid [32]. Alkyds tend to be lower in cost than most other vehicles and tend to give coatings that exhibit fewer film defects during application [33].

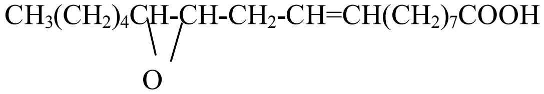
1.3.1 Raw material selection

Alkyds are derived from three different materials; drying/semidrying oils, polyol, and dibasic acid. Oils are obviously very important for alkyd resin performance; however careful selection of the polyol and dibasic acid used for synthesis is equally as important. Several factors need to be considered, such as material cost, material availability and reaction rates. Material selection is also important to the overall performance of the resulting film and the final cost of the coating.

1.3.2 Fatty acids and Oil

Oils and fats are very much part of daily life. Although fats are solids and oils liquids, both share the same basic organic structure which are glycerol esters (glycerin) and are also termed triglycerides. When heated in presence of an alkali, glycerol and a mixture of fatty acids are produced. The most common fatty acids in natural oil compositions are given in Table 1.1. [34]. As shown, some fatty acids are saturated and some of them are unsaturated. Unsaturated fatty acids have one or more double bonds.

Table 1.1 : Some fatty acid compositions in natural oils [34]

Name	**Formula**	**Structure**
Myristic acid	$C_{14}H_{28}O_2$	$CH_3(CH_2)_{12}COOH$
Palmitic acid	$C_{16}H_{32}O_2$	$CH_3(CH_2)_{14}COOH$
Palmitoleic acid	$C_{16}H_{30}O_2$	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$
Stearic acid	$C_{18}H_{36}O_2$	$CH_3(CH_2)_{16}COOH$
Oleic acid	$C_{18}H_{34}O_2$	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
Linoleic acid	$C_{18}H_{32}O_2$	$CH_3(CH_2)_4CH{=}CH\text{-}CH_2\text{-}CH{=}CH(CH_2)_7COOH$
Linolenic acid	$C_{18}H_{30}O_2$	$CH_3\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH{=}CH(CH_2)_7COOH$
α-Eleostearic acid	$C_{18}H_{30}O_2$	$CH_3(CH_2)_3CH{=}CH\text{-}CH{=}CH\text{-}CH{=}CH\ (CH_2)_7COOH$
Ricinoleic acid	$C_{18}H_{33}O_3$	$CH_3(CH_2)_4CH\text{-}CH(OH)\text{-}CH_2\text{-}CH{=}CH(CH_2)_7COOH$
Vernolic acid	$C_{18}H_{32}O_3$	 $CH_3(CH_2)_4\underbrace{CH\text{-}CH}_{O}\text{-}CH_2\text{-}CH{=}CH(CH_2)_7COOH$
Licanic acid	$C_{18}H_{28}O_3$	$CH_3(CH_2)_3CH{=}CH\text{-}CH{=}CH\text{-}CH{=}CH(CH_2)_4(CO)\text{-}(CH_2)_2COOH$

Additionally, some natural fatty acids have different structure, with acid chains having hydroxyl, epoxy or oxo groups or triple bonds. Because of their structural differences, each fatty acid has various physical properties.

Castor oil is one of the vegetable oils which received particular attention since ricinoleic acid (87.5%), its principal constituent, has a secondary alcohol function and unsaturated bond. This hydroxyl group can be dehydrated to give an extra double bond directly during the manufacture of the alkyd resin [35].

The fatty acid distribution of several common oils is shown in Table 1.2. [34]. There are many examples of synthesis of different kinds of polymeric resins made from seeds and oils of plants. Dutta et al. [36] used Nahar seed oil to synthesize polyester resin. Other traditional seeds such as linseed [37], soybean [38-40], amaranth [41], castor [42-44], sunflower kernels [45] cashew nut [46, 47] tall oil [48] have been used or still under development for the synthesis of different kinds polymeric resin.

Table 1.2 : Some fatty acid distribution in several common natural oils (%) [34]

Fatty acid	**Castor oil**	**Linseed oil**	**Oiticica oil**	**Palm oil**	**Rapeseed oil**	**Tall oil**	**Soybean oil**	**Sunflower oil**
Palmitic acid	1.5	5	6	39	4	4	12	6
Stearic acid	0.5	4	4	5	2	3	4	4
Oleic acid	5	22	8	45	56	46	24	42
Linoleic acid	4	17	8	9	26	35	53	47
Linolenic acid	0.5	52	-	-	10	12	7	1
Ricinoleic acid	87.5	-	-	-	-	-	-	-
Licanic acid	-	-	74	-	-	-	-	-
Other	-	-	-	2	2	-	-	-

1.3.2.1 Palm oil production

Palm oil is one the most widely used plant oils in the world which is grown in tropical countries. It originates from West Africa and was introduced to Malaysia at the beginning of the 20th century and commercially produced in 1917. Malaysia is one the largest producers and exporters of palm oil in world. Table 1.3 compares the historical growth in world production of oils and fats with palm oil. Tallow and coconut oils have been the predominant raw materials for oleochemicals; tallow as a major source of C_{16}-C_{18} fatty acids and coconut oil for C_{12}-C_{14} fatty acid [49].

World production of palm oil in 1989 was 10.3 million tones, which represents an almost eleven-fold increase since 1950: during the same period, the production of soya bean oil increased by a factor of seven and that of tallow oil by a factor of only three, while the increase in world production of palm kernel oil was two times of coconut oil. The growing importance of palm and palm kernel oils in the world's oils and fats scene is indicated in the increase in their production up to the year 2000.

Table 1.3 : World productions of oils and fats suitable as raw materials for oleochemicals (Million tones) [49].

Oils and Fats	**1950**	**1960**	**1970**	**1980**	**1989**	**1990**	**1995**	**2000**
Soya Bean	2.1	4.0	6.1	12.2	15.0	16.1	18.2	21.0
Tallow	2.2	3.6	4.4	6.0	6.6	6.6	7.1	7.0
Coconut	1.9	2.1	2.2	3.3	2.8	3.1	3.8	4.2
Palm	0.9	1.1	1.7	5.0	10.3	10.8	17.8	22.0
Palm Kernel	0.4	0.4	0.4	0.7	1.3	1.4	2.3	2.8
Others	16.1	20.9	25.3	29.6	41.3	41.2	35.2	50.0
Total	23.6	32.1	40.1	56.8	77.3	79.2	84.4	107

The oil palm is one of the world's most economical oil crops. A tonne palm fruit known as fresh fruit bunches (FFB), can yield 200 kg of crude palm oil and 40 kg of palm kernels, which in turn yield about 50% or 20 kg of palm kernel oil. A hectare of land can yield 20-24 tonnes/ year of FFB. Thus a hectare yields 400-500 kg of palm kernel oil and four to five tonnes of palm oil annually [50].

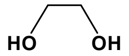
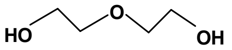
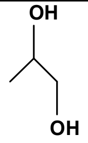
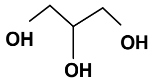
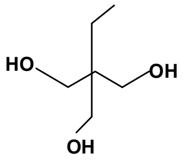
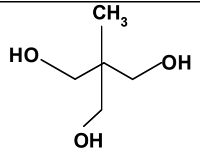
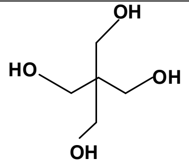
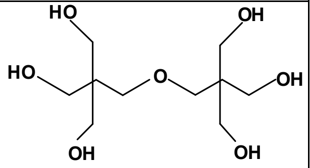
Prior to 1980, palm kernel oils and palm were mainly used, after refining and fractionation, for edible purposes. Since the development of the Malaysian oleochemical industry in the early eighties, there has been an increase in use of these oils as raw materials for oleochemical production. In 1989, Malaysia was responsible for almost 60% of the world production of palm and palm kernel oils, while ASEAN (the Association of South-East Asian Nations) produced 75% of the world output of palm and lauric oils (palm kernel and coconut oils). There are many applications where palm and palm kernel based oleochemicals excel as replacements for those made from tallow and coconut oils. Some of these are cosmetics, soaps, pharmaceuticals, textile lubricants, paints, candles and biocides as well as applications in road making, plastics and rubber industries. Its non cholesterol quality and digestibility make it desirable as source of energy, while its economic and technical superiority makes it preferable as based material in the manufacture of various non-edible products. It can also be used to produce polyol and first produced by the Malaysian Palm Oil Board (MPOB) from epoxidized palm oil [51].

1.3.3 Polyols

Many various chemical compounds are used as polyalcohol (polyols) in the preparation of alkyd resins. Some common polyalcohols used for synthesis of alkyd are tabulated in Table 1.4. Ethylene glycols have only two hydroxyl groups and used to formulate unmodified resins which are linear thermoplastics and can only be crosslinked with unsaturated polyesters. Longer chain glycols, such as diethylene glycol and propylene glycol will only provide the finished resins with greater flexibility. Glycerol is a triol and the most widely used polyol because it is present in naturally occurring oils from which alkyds are commonly synthesized. Due to its trifunctionality, glycerol is able to add more branching in the alkyd macromolecule, providing a three-dimensional polymeric network and thus results a high molecular weight resin. Table 1.4 shows that this polyol has two kinds of hydroxyl group with different reactivity.

All the three hydroxyl groups react almost the same rate with fatty acid at 180-260˚C, but with dibasic acids such as phthalic, α-hydroxyl groups are more reactive than the β-hydroxyl groups [52].

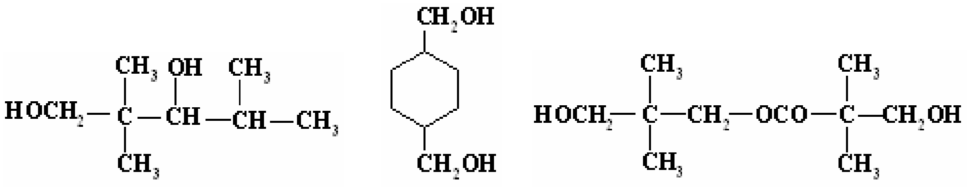
Table 1.4 : Some common polyalcohols used to synthesize of alkyd

Polyhydric alcohol	**Formula**	**Structure**
Ethylene glycol	$HO(CH_2)_2OH$	
Diethylene glycol	$HO(CH_2)_2O(CH_2)_2OH$	
Propylene glycol	$CH_3CH(OH)CH_2OH$	
Glycerol	$HOCH_2CH(OH)CH_2OH$	
Trimethylolpropane	$CH_3CH_2C(CH_2OH)_3$	
Trimethylolethane	$CH_3C(CH_2OH)_3$	
Pentaerythritol	$C(CH_2OH)_4$	
Dipentaerythritol	$[(CH_2OH)_3CCH_2]_2O$	

The glycerol when used in the monoglyceride phase, at a temperature ranging from 260-290˚C, it can dehydrate leading to formation of acrolein. Not only is acrolein an irritant and very lachrymatory, it also reduces the quantity of glycerin available for the transesterification reaction. At higher temperature, it is replaced by trimethylolpropane.

Pentaerythritol, has four primary reactive hydroxyl groups. Alkyd paints made with pentaerythritol, have superior adhesion, weather-resistance, water resistance, luster, chemical resistance and rapid drying properties in comparison with trihydric alcohols, such as glycerol. Because of the four reactive hydroxyl groups, it forms a much more complex resin with phthalic anhydride than with glycerol. Pentaerythritol is used essentially in long oil alkyd resins as the long and middle oil lengths having fatty acid content about 65-70%, are commercially available. If pentaerythritol is mixed with a dihydric alcohol then, it may be used in short oil alkyds [53]. The four hydroxyl groups in pentaerythritol structure are equivalent in reactivity. This polyol behaves more uniformly due to its symmetrical structure compared to glycerol.

In choosing polyols, three factors affect durability. Both steric factors and the 'neighbouring group' or 'anchimeric' effects influence resistance to hydrolysis [54]. The absence of hydrogen atoms on the carbon atom beta to the hydroxyl group and subsequent ester group is a principal factor determining resistance of the ester link to break down under the influence of heat or radiation. These requirements are met by such polyols as 1,4-cyclohexanedimethanol (CHDM) and 2,2,4-trimethyl-1,3-pentane diol (TMPD) where the beta hydrogen content is reduced or hindered in materials such as hydroxypivalyl hydroxy pivalate (HPHP). Figure 1.2 demonstrates typical polyol structures with hindered beta positions relative to OH group. The above polyols (Table 1.4) are the widely used, mostly because of low cost and availability, but other polyols are normally used either in small amounts or for very specific applications.



(TMPD) (CHDM) (HPHP)

Figure 1.2: Typical polyol structures with hindered β positions relative to OH group.

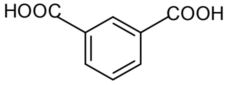
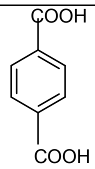
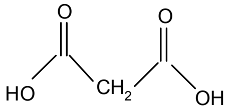
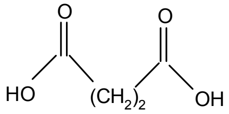
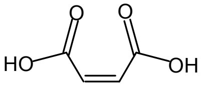
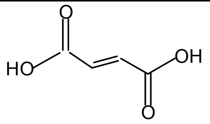
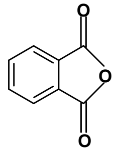
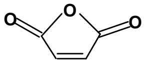
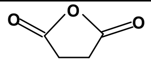
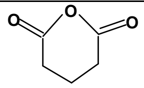
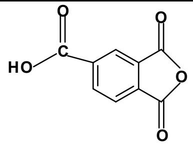
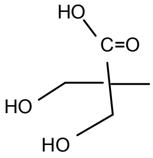
1.3.4 Polybasic acids

A number of polyacids have also been recommended for preparation of alkyds. The most important and common polybasic acids used for synthesis of alkyd are listed in Table 1.5. Dibasic acids used to prepare alkyds are usually aromatic and their rigid aromatic rings increase the T_g value of the resin. Cycloaliphatic anhydrides, such as succinic anhydride and glutaric anhydride, may also be used. While they are not as rigid as aromatic rings, the cycloaliphatic rings also increase the T_g value.

By far, the most widely used dibasic acid is phthalic anhydride (PA). It has the advantage that the first esterification reaction precedes rapidly by opening the anhydride ring. As a result the amount of water evolved is lower and also reduces reaction time. Phthalic anhydride gives alkyd resins with hardness and chemical resistance, due to the phenyl group's resistance to rotation. The relatively low melting point (the pure compound melts at 131˚C) is desirable, since the crystals melt and dissolve readily in the reaction mixture.

In the large-scale manufacturing, molten PA is used which reduces packaging, shipping and handling costs. Unsaturated polybasic acids and their anhydrides could form hydrogen bond among molecules and also provide higher tackiness to the final alkyd.

Table 1.5 : Some common polybasic acids used to synthesize of alkyd

Polybasic acid	**Formula**	**Structure**
Isophthalic acid	$C_8H_6O_4$	
Terephthalic acid	$C_8H_6O_4$	
Succinic acid	$C_3H_4O_4$	
Adipic acid	$C_4H_6O_4$	
Maleic acid	$C_4H_4O_4$	
Fumaric acid (FA)	$C_4H_4O_4$	
Phthalic anhydride (PA)	$C_8H_4O_3$	
Maleic anhydride (MA)	$C_4H_2O_3$	
Succinic anhydrid	$C_4H_4O_3$	
Glutaric anhydrid	$C_5H_6O_3$	
Trimellitic anhydride (TMA)	$C_9H_4O_5$	
Dimethylolpropionic acid (DMPA)	$C_5H_{10}O_4$	

The next most widely used dibasic acid is isophthalic acid (IPA). Esters of IPA are more resistant to hydrolysis than those of PA in the pH range of 4-8 (the most important range for exterior durability). On the other hand, under more alkaline conditions esters of phthalic anhydride are more resistant to hydrolysis than isophthalic esters. The raw material cost for IPA is not particularly different from PA, but the manufacturing cost is higher. The high melting point of IPA (330˚C) leads to problems of getting it to dissolve in the reaction mixture so that it can react [55]. The longer time at higher temperature also leads to greater extent of side reactions of the polyol component [56].

Maleic anhydride (MA) acid is sometimes used with PA. The use of MA gives notable importance in the drying properties, hardness and colour of the resin. It is often used to effectively increase the viscosity of a resin which will then require a large volume of dilution solvent, thus reducing the cost of the alkyd. However, the replacement of PA by MA in excessive amounts may leads to gelation during synthesis. Aliphatic acids, such as succinic acids and adipic, are sometimes used as partial replacements for PA to give more flexible films.

Other polybasic acid often used in smaller quantities is fumaric acid (FA), which requires a higher processing temperature for solubility and releases additional water during the reaction. These dibasic acids (MA and FA), beside their function as dibasic acids, can also be used to increase the functionality of the resin through the reaction with the unsaturated bonds in fatty acids, terpenes, rosin, etc. Thus the replacement of PA with MA produces a more complex molecular structure with higher viscosity, and gelation may occur. In normal alkyd production, MA or FA inclusion is usually restricted to 1-10% of the PA content. Trimellitic anhydride (TMA) as a tribasic acid is frequently used for water soluble alkyds, since it gives a free carboxyl function which is readily accessible to an amine for neutralisation. It is also used high solid alkyds.

Dimethylolpropionic acid (DMPA) with a diol function in its molecule is employed for esterification reactions leaving the acid functionality free. The preparation of water-dilutable alkyd resins from DMPA is of high quality to those obtained with TMA. It remains, however, a very expensive product for the alkyd resins industry.

1.4 Classification of alkyd resins

Because alkyds are a large and diverse family of resins, several categories are used to classify alkyd resins. Further classification is based on the ratio of monobasic fatty acids to total weight of polymer formed during synthesis. The terminology used to describe this classification is oil length of an alkyd. The oil length of an alkyd is calculated using equations [1.1], [1.2] and is expressed as a percentage [57].

$$\text{Oil length} = \frac{\text{Weight of oil}}{\text{Weight of alkyd} - \text{Water evolved}} \times 100 \qquad [1.1]$$

$$\text{Oil length} = \frac{1.04 \times \text{weight of fatty acid}}{\text{Weight of alkyd} - \text{Water evolved}} \times 100 \qquad [1.2]$$

The 1.04 factor in equation [1.2] converts the weight of fatty acids to the corresponding weight of triglyceride oil. Oil length is an important factor, which affects the properties of the final product. Alkyd resins based on oil length are divided by three categories [53].

Long oil length alkyds: air drying and aliphatic solvent compatible. Long oil alkyds, containing > 55% of a drying oil, are used in building interiors. Other applications which are still widely used include marine and maintenance applications as primers and finishes.

Advantages: Air drying in 5 to 8 hours, low viscosity, excellent gloss and wetting of pigments.

Disadvantages: Poor hardness, poor exterior resistance and solvent, alkali, and hydrocarbon sensitive.

Medium oil length alkyds: air and oven drying; aliphatic and aromatic solvent compatible. Medium oil alkyds, containing 40-55% of oil, are often used in low cost anticorrosion primers and some industrial stoving enamels such as agricultural machinery.

Advantages: Air drying in 3 hours, rather high viscosity, induced or assisted air drying (50-80°C) and good gloss. Medium oil alkyds can be used in paints along with long oils to improve metal adhesion of the long oils.

Disadvantages: poor hardness, hydrocarbon, alkali and oil sensitive.

Short oil length alkyds: air and oven drying; aromatic hydrocarbon and ester solvent compatibility. It contains < 40% oil and applied in industrial coating sector as anti-corrosive primers and finishes. Other applications are; stoving enemals, agricultural machinery finishes, commercial and car refinishes.

Advantages: Good substrate adhesion and hardness, flexible, water and weathering resistance.

Disadvantages: Limited compatibility with many aliphatic (low toxicity) solvent

Figure 1.3 depicts effect of oil length and degree of unsaturation (Iodine Value) on the properties of alkyd resin [58]. The long oil length alkyd indicates oil-like properties, where they are softer, having higher flow ability and form coating with lower level of tackiness, whereas the medium oil length alkyd corresponds to an even weight mixture of resin-like and oil-like properties. The short oil length alkyd shows resin-like properties which have higher viscosity, tackiness and impart the hardness of a coating.

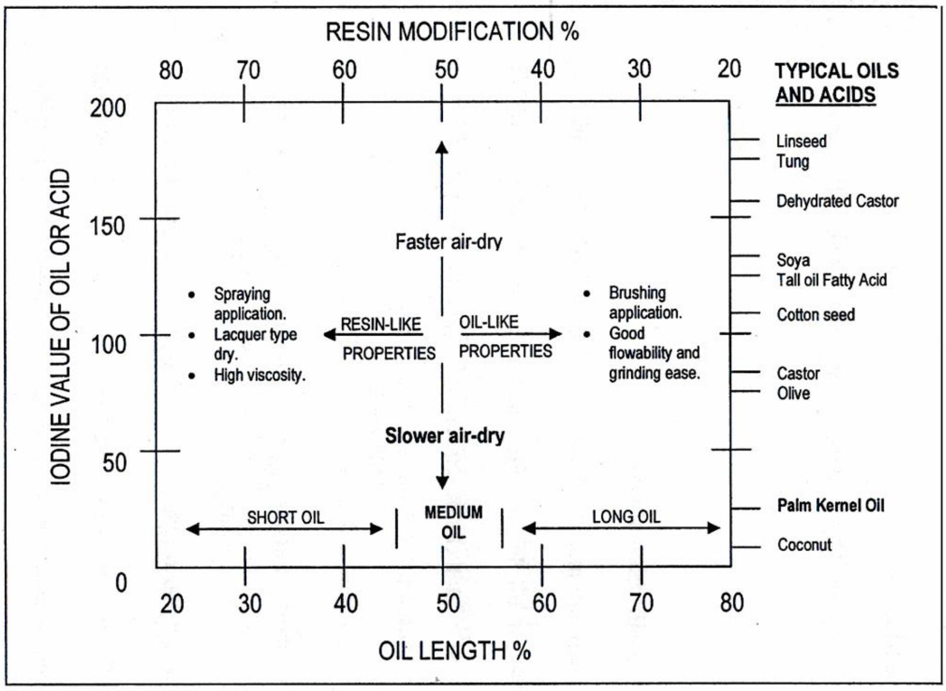


Figure 1.3: Effect of oil length and degree of unsaturation (Iodine Value) on the properties of alkyd resin [58]

A second system classifies alkyd into oxidizing and non-oxidizing types [59]. An oxidizing alkyd contains drying (unsaturated) or semi-drying oils or fatty acids and is able to form film by air oxidation. This type of alkyd usually has an oil length in excess of 45%. A non-oxidizing alkyd contains non-drying (saturated) oils or fatty acids and therefore the alkyd is not capable of forming coherent film by air oxidation. Hence, the non-oxidizing alkyd is used as polymeric plasticizer or as hydroxyl-functional resin, which are cross-linked by melamine-formaldehyde or urea-formaldehyde resin, or by isocyanate cross-linker. The oil length for non-oxidizing alkyds usually is below 45%.

1.5 Synthesis of alkyd resin

Various synthetic procedures, each with many variables, are used to produce alkyd resins [55, 60]. Alkyd resins are prepared by the polycondensation of polyols and polyacids until predetermined values for viscosity, acid value or theoretical water loss are obtained. Alkyds can be made directly from oils or by free fatty acids. The properties of formulated alkyd resin, depends on the chemical composition and also their preparation processes [53, 59].

1.5.1 Monoglyceride process (Alcoholysis)

The first option, known as the monoglyceride process, is typically used when glycerol is the polyol of choice [59]. Oils are naturally available as triglycerides of fatty acids. In the monoglyceride process, alkyds are synthesized in a two step procedure. Since PA is soluble in the glycerol, but is not soluble in the oil, transesterification of oil with glycerol must be carried out to overcome of incompatibility as a distinct and separate step in presence of a catalyst at temperatures 225-250˚C, before the PA is added. In this step of reaction, polyol and glyceride oil convert into a single homogenous monoglyceride phase; otherwise, glyceryl phthalate gel particles would create in early stage of the process. The next step of this reaction is esterification by polyacid and the remainder of the polyol in order to complete the alkyd reaction. This process is usually applied when PA is used as the polybasic acid. The monoglyceride process is shown schematically in Figure 1.4.

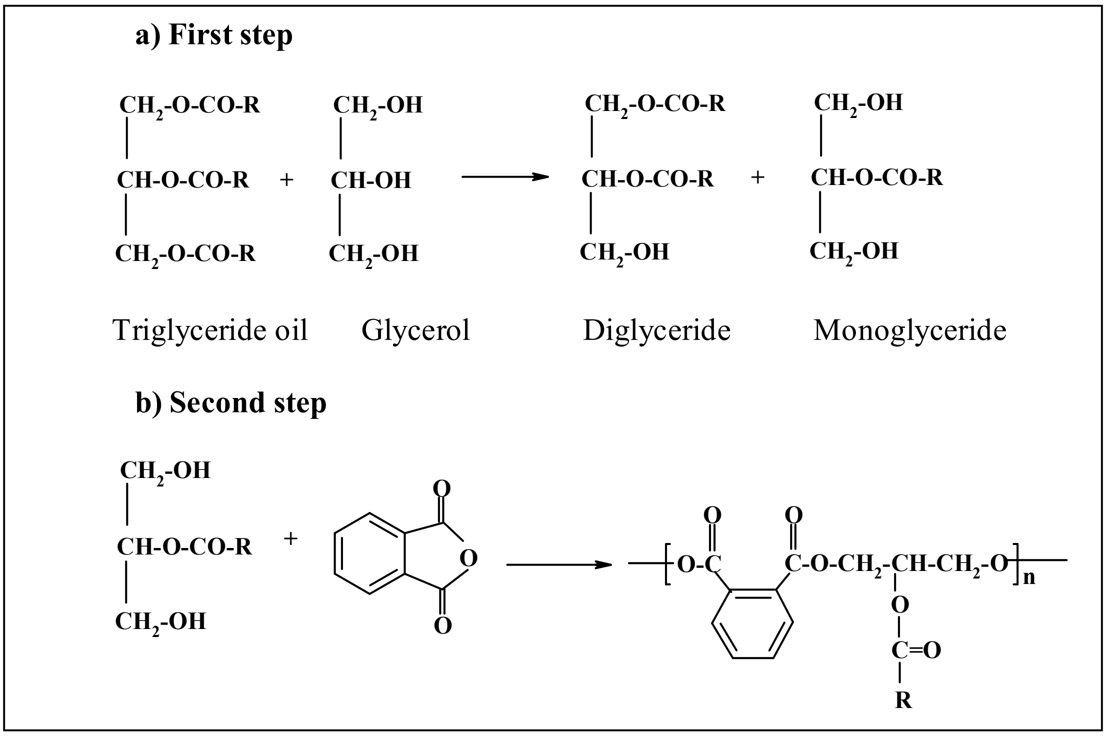


Figure 1.4: Preparation of alkyd resin by monoglyceride process

While the process is called the monoglyceride process, the transesterification reaction actually results in a mixture of unconverted drying oil, monoglyceride, unreacted glycerol and diglycerides. The composition depends on the ratio of glycerol to oil and on time, kind and amount of catalyst and temperature. The viscosity and properties of alkyd can be affected by the extent of reaction before PA addition.

1.5.2 Fatty acid process

In this case, fatty acids are used instead of oils. This technique is the quickest since all the raw materials are compatible. Additionally, this technique can produce alkyds in various methods. The three simplest and the most common methods are being described as follows:

The first procedure can be carried out in a single stage where all the raw materials, fatty acid, polybasic acid and polyhydric alcohol, are added together at the beginning of the reaction and the esterification takes place simultaneously in temperature range of 220-240°C. Thus, due to free competition among the hydroxyl and carboxylic groups an alkyd with more branching is synthesized.

The second procedure can be performing in two stages. The polyhydric alcohol (glycerol) and polybasic acid (PA) are first reacted together at 180°C until a clear viscous resin is obtained. The reaction is followed with adding warm fatty acids and the temperature is increased to 180-220°C. In this case, the carboxylic groups of PA are deliberately reacted with the primary hydroxyl groups of glycerol to form glycerol phthalate before fatty acid is added. Therefore, the carboxylic groups of fatty acid are forced to esterify with the leftover hydroxyl groups of glycerol phthalate. Hence, the alkyd's structure is linear [60].

The third procedure is conducted under a stepwise addition of fatty acids from 40-90%, at 180-250°C. This procedure has been modified by Kraft [61] and is often called the high polymer technique. This involves the incremental addition of a portion of the monobasic acid to the polymer. Adding of the monobasic acid gradually reduces the chain-terminating reactions in early stages of polymerization process and increase high molecular weight polymers. This imparts faster drying time and better chemical resistance to the resin obtained. The comparisons of the characteristics of the two processes are tabulated in Table 1.6.

Table 1.6 : Characteristics of the alkyd synthesis procedure [61]

Procedure	Characteristics
Fatty acid	1) It enables better control of the reaction as well as greater freedom for the formulator. Better formulation flexibility, since any polyhydric alcohol or blend can be used. 2) The reaction can be started by reacting the polyol with the diacid to the desired condensation level and then esterifying the polyol with the fatty acid, corresponding to the so-called “high polymer” process. 3) Alkyd resins are thereby obtained with high viscosity, improved drying and hardness properties. 4) This process does not need a catalyst and consequently oxidation and colour problems can be eliminated. 5) The resulting alkyd tolerates less aliphatic hydrocarbon thinner compared to monoglyceride method. 6) Low acid value is more rapidly reached.
Monoglyceride(Alcoholysis)	1) The alkyd tends to be marginally softer and tackier. 2) This process needs a catalyst and consequently causes oxidation and colour problems. 3) The rate of esterification slows down at higher acid value. 4) The alkyd tolerates more aliphatic hydrocarbon thinner.

1.6 Process variations

In esterification, the rate of removal of water from the reactor is an important factor that affects the reaction rate, being a reversible reaction.

Generally, esterification reaction includes two steps. These steps are demonstrated in Figure 1.5. Esterification is carried out rapidly by opening the anhydride ring in the initial stage, lowering the temperature which caused the formation of half-esters. In this step, no water of reaction evolved. The second stage of the reaction continues by increment of the temperature and long chain molecules are produced which contain free excess hydroxyl groups. At this stage the water of reaction is released.

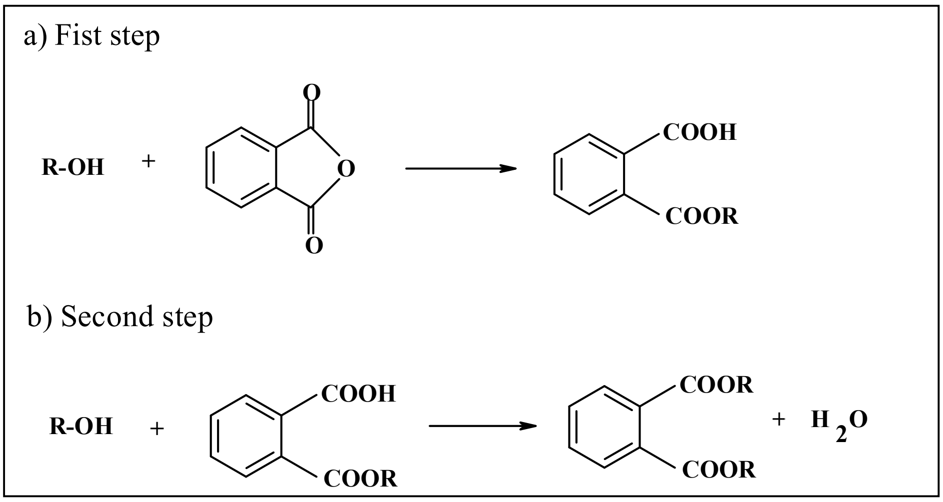


Figure 1.5: The esterification reaction for the alkyd preparation by dibasic acid anhydrides.

In order to remove the water of reaction two methods i.e. solvent cook and fusion are applicable. We can add some solvent which boils off as vapour and carries off the water facilitating the removal of the water. These mixed vapours can then be condensed and collected. By choosing the correct solvent that does not mix with water in liquid state- the mixture can now be separated in two layers, the lower water layer decanted off and the original entraining liquid returned to the kettle. Aromatic hydrocarbons are water-insoluble, so that separation of water phase from the organic phase occurs very rapidly and the organic phase can be recycled immediately to the reactor. Aromatic hydrocarbons dissolve

PA which sublimates on the cool portions of the reactor and leads to a substantial reduction in its loss from the system. By using this technique (azeotropic process) the amount of inert gas needed can considerably be reduced. Xylene is the most suitable solvent for this process as it has a suitable boiling point and low water solubility [62].

With the fusion method there is some volatilisation of components of the batch. During the monoglyceride or alcoholysis stage, there is some decomposition of the oil. In the fusion process these products, along with some polyols, are carried away through ducting. Even with the solvent process these products are soluble in the solvent or condense in the condenser or separator which can cause fouling. The polyols are usually soluble in the water and the formulation needs to be adjusted to compensate for these losses.

1.7 Estimation of progress of reaction

A critical aspect of alkyd synthesis is deciding when the reaction is completed. The progress of reaction is monitored by periodically checking of acid number and viscosity. In fact, the disappearance of carboxylic acid is followed by titration and the increase in the molecular weight is followed by viscosity.

Many variables affect the acid number and viscosity of alkyds. One is the ratio of reactants. The greater the ratio of hydroxyl groups to carboxylic acid groups, the faster the acid groups are reduced to a low level. The degree of completion of the reaction is an important factor controlling the viscosity, as well as acid number. It is usually desirable to have a low acid number.

The composition of the fatty acids and oils are also major factor affecting the viscosity. Some volatilization of polyol, PA and fatty acids out of reactor which will occur depending on the design of the reactor, the rate of reflux of the azeotroping solvent, the rate of inert gas flow and the reaction temperature are other variables; the amount and ratio of these losses affect the viscosity and acid number. On the other word, side reactions can affect the viscosity-acid number relationship. Glycerol and other polyols form ethers to some degree during the reaction (under high temperature). When these reactions occur, the mole ratio of dibasic acid to polyol increases and the number of hydroxyl groups decreases; therefore, at the same acid number the molecular weight will be higher [63].

1.8 Classification of polymers by the kinetic mechanism

Monomers can be combined into polymeric chains by different chemical procedures. According to the polymer chain growth mechanism, polymerization can be classified into two major categories: chain-growth (addition polymerization) and step growth polymerizations.

1.8.1 Free radical polymerization

Free-radical polymerization, commonly attributed to addition polymerization is one of the chemical processes that alter monomer into long chain segments. Careful control of molecular weight can be achieved in these syntheses by complete understanding of reaction kinetics. The lifetime of polymer chain is of the order of 0.1-1.0 second. This means that high molecular weight polymer is formed from beginning of the polymerization [64].

Acrylic alkyd hybrid materials can be synthesized through this type of polymerization by introducing free radicals in the presence of acrylic monomers and alkyd resin. Three kinds of chemical reactions, initiation, propagation, and termination are always involved. Monomers polymerized by this process must contain an unsaturated site in their structure. The reactivity exhibited by the two electrons in the π-bond found on the doublybound carbon atoms is the fundamental factor that gives monomers the ability to experience the chain growth phenomena [65].

In order for polymerization to occur, a free radical initiator must break into free radicals to begin the process. Once monomer units add rapidly, high molecular weights of polymers build up in a short time unlike step-growth polymers. As noted earlier free-radical polymerization is separated into three distinct steps. The first step occurs when the free radical initiator dissociates to produce free radicals. Initiation involves another reaction, the addition of the first monomer unit to form the initiating species. The general equations to represent these steps in the initiation are as follows, where I is the initiator, R• the initiating species and M the monomer unit:

$$\mathbf{I} \quad \rightarrow \quad \boldsymbol{2R\bullet}$$

$$\boldsymbol{R\bullet + M \rightarrow RM\bullet}$$

The next step of chain-growth polymerization includes the addition of monomer units to the initiating species until the radical reactive centre is transferred to the end of the propagating chain. This portion of the polymerization is ascribed to as the propagation step and can be described by the following equations, where M is the monomer and ~ • is characteristic of a growing polymer chain, and k_p is the constant rate for propagation:

$$\boldsymbol{RM\bullet + M \rightarrow RMM\bullet}$$

$$\boldsymbol{RMM\bullet + M \rightarrow RMMM\bullet}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\sim^{\bullet} + \boldsymbol{M} \xrightarrow{k_p} \boldsymbol{\sim M\bullet}$$

The third step of free radical polymerization is termination step. Finally, the special chains will stop growing. Termination of the growing radicals is attained in one of two ways. Two growing chains contain radicals may react with each other by combination resulting in “dead” polymer or more rarely, by disproportionation, in which hydrogen radical that is beta to one radical centre is transferred to another radical centre. These result in the formation of two polymer molecules; one saturated and one unsaturated [66]. The equations for termination reactions are as follows; where k_{tc} is the constant rate of radical-radical termination by combination, ***GPH*** is a growing polymer chain and k_{dis} is the constant rate of disproportion:

$$\sim^{\bullet} + \sim^{\bullet} \xrightarrow{k_{tc}} \textbf{\textit{Dead Polymer}}$$

$$\sim^{\bullet} + \bullet \boldsymbol{GPH} \xrightarrow{k_{dis}} (\textit{Saturated polymer}) \sim \boldsymbol{H} + \boldsymbol{GP}\ (\textit{Unsaturated polymer})$$

The term dead polymer represents the stopping of growth for the propagating radical. The propagating reaction would continue to until all monomers in the reaction system were exhausted.

When highly reactive species like free radicals are included, side reactions also occur. The chain-transfer reactions are one of the side reactions, in which the free radical on the end of the propagating polymer chain abstracts a hydrogen atom from some substance such as molecule of the solvent, a molecule of polymer, X-H, that exists in the polymerization reaction mixture, as shown below:

$$\text{X-H} + \sim \boldsymbol{M}\bullet \rightarrow \text{X}\bullet + \sim \boldsymbol{M}\mathbf{H}$$

The effect of chain transfer is to terminate the growing chain and generate a new free radical that can start a second chain growing.

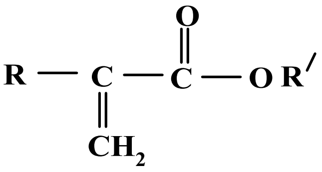
1.8.2 Step growth polymerization

Step growth polymerization is the second type of the polymerization that has actual importance in coating. The principles of step-growth polymerization were first studied by Carothers and Flory [67, 68]. Flory established many of the basic principles of polymer science through detailed studies on polyester systems. These basic principles, defined over half a century ago still remain as a basis for polymer chemists today. Esterification is one of class of reaction that can be applied in step growth polymerization. The term condensation polymerization has also been widely used for this process due to condensation reactions in which small molecule by product, such as water, is evolved. The life time of a growing polymer chain is of the order of hours. This means that the polymer molecular weight rises diligently throughout the polymerization [67]. If, a chain-growth polymerization is stopped before the reaction has gone to completion, the reaction mixture will comprise of high molecular weight polymer and unreacted monomer. However, if a step-growth polymerization is stopped at a similar stage, the reaction mixture will consist of mainly relatively low molecular weight reaction products and monomer with very little high molecular weight polymer.

All of the monomers must have two or more functional groups to be able to synthesize by step growth polymerization. When monomers have two functional groups, linear polymers will form. Step growth polymerization reactions are used to synthesize the resins for use as coating materials.

1.9 Monomer selection

Acrylic monomers utilized in copolymer formulations provide individual contributions to the overall performance of the final coating. Acrylic monomers also provide the final coating with flexibility, hardness, water resistance, scratch resistance, exterior durability, tensile properties, solvent resistance and adhesion. A typical structure of an acrylic monomer is shown in Figure 1.6.



$$R-\underset{\underset{CH_2}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OR'$$

R=H, $-CH_3$

R' = H, $-CH_3$, $-CH_2CH_3$, $-(CH_2)_3CH_3$

Figure 1.6 : A typical structure of an acrylic monomer

Methacrylic ester monomers are a versatile group of monomers whose physical and chemical properties depend upon the "R' " group, the molecular weight and the tacticity of the polymer [69], the number of carbon atoms present in the backbone and the nature of the substituent present on the α position of the vinyl group polymer [70]. Methacrylic monomers differ from acrylics in that they have a methyl group in α position of the vinyl group; this methyl group helps in the stability, hardness and stiffness of the polymers formed from the methacrylic ester monomers. Methacrylics will readily polymerize with other methacrylic and acrylic monomers. Although more costly than many other commonly employed industrial monomers, methacrylics have found a great deal of industrial usage because of their unique balance of performance properties as well as their ease of use. These polymers find applications that range from extremely tacky adhesives to hard powders and sheets. Generally, in hybrid resins that contain acrylic polymers, the side chain composition and chain length of each monomer also provide unique film properties. Tables

1.7 and 1.8 represent the properties that each monomer adds to the final resin. Formulations of acrylic monomers are chosen based on these properties [71].

Table 1.7 : Properties contributed by common acrylic monomers

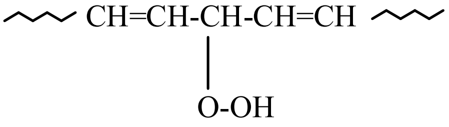
Film Property	**Contributing Monomers**
Hardness	Methyl methacrylate
Flexibility	Butyl acrylate, methacrylic acid, acrylic acid and ethyl acrylate,
Exterior Durability	Methacrylates and acrylates
Water Resistance	Methyl methacrylate, acrylates
Scratch Resistance	Acrylate and short chain methacrylate

Table 1.8 : Effect of side chain groups on polymer properties

Property	**MMA**	**EA**	**BA**	**HEA**
Hardness	Hard	Soft	Very Soft	Very Soft
Tensile Strength	High	Low	Very Low	Extremely Low
Tackiness	Tack free	Tacky	Very Tacky	Extremely Tacky
Elongation	Low	Very High	Extremely High	-
Solvent Resistance	Excellent	Very Good	Fair	Low
UV Stability	Excellent	Fair	Good	Good
Gloss Retention	Excellent	Good	Fair	Poor

1.10 Alkyd based coatings

Alkyd based coatings are one the most common binders used for ambient-cure, solvent-based coatings and have several advantages including high gloss, good colour retention, good heat and autoxidative crosslinking mechanism [72]. The resistance properties of traditional solvent-borne alkyds are developed via autoxidative crosslinking of the alkyd film. Crosslinking occurs when the activated methylene groups in the unsaturated fatty acids or oils of the alkyd are oxidized in air to give hydroperoxides which subsequently decompose by heat or light to generate free radicals, resulting in oxidative crosslinking. A plausible structure of hydroperoxide formed on an allylic methylene group is shown in Figure 1.7 below:



$$\sim\sim\ \mathrm{CH{=}CH{-}}\underset{\underset{\mathrm{O{-}OH}}{|}}{\mathrm{CH}}\mathrm{{-}CH{=}CH}\ \sim\sim$$

Figure 1.7 : Typical structure of hydroperoxide

An autoxidation of alkyds is a chain reaction that proceeds by a free radical mechanism. The free radical hydroperoxide ($ROO^{\bullet}$) is capable of several further reactions; some of them lead to formation of stable, covalent bonds with sites on other molecules. These bonding may build up a three dimentional network to form a tough film. Fatty acid chains containing only one double bond such as oleic acid autoxidizes slowly. While those containing allylic methylene groups activated by two double bonds react over 100 times faster. There are some disadvantages which include poor water and acid retention, and alkali resistance [72].

Alkyds are generally deficient with respect to hydrolytic stability and typically require the use of organic solvents to achieve manageable viscosities due to the long hydrocarbon chains introduced by the pendant fatty acids. Over the years, several approaches have been used to achieve greater hydrolytic stability of alkyd resins [73, 74]. One approach is reacting monoglyceride with carboxylic acid groups. Another method for achieving modified alkyd of this type is by reacting a completed alkyd (acid value < 10 mg KOH/ g sample) with maleic anhydride [75]. The modification of alkyd resins by acrylation for enhancing their properties has been also extensively investigated. Various methods have been employed by researchers for such chemical modifications. By careful selection of monomers used in the acrylic portion of the formula, the hydrolytic stability and speed of drying process can be adjusted. Much work has also been carried out in this area by researchers to understand effect of monomer conversion, effect of the alkyd ratio and crosslinking levels on the film properties [76, 77].

The synthesis of acrylated alkyd was first attempted by F. Armitage and S. Kut [78]. Synthesis of acrylate modified alkyds using esterification reaction between anhydride, carboxyl or epoxide groups in performed copolymer and hydroxyl and carboxyl groups of alkyds have been extensively reported by D.H. Solomon and co-workers [79-82].

Akintayo and Adebowale modified an Albizia benth medium oil alkyd by acrylation to form hybrid resins [83]. They used n-butylmethacrylate (n-BMA) and MA at different ratios to prepare carboxy-functional acrylic copolymers. The performed copolymers were then used to synthesize the methacrylated albizia benth medium oil alkyds by solution method in xylene. Results revealed that the acrylated resin exhibited improved characteristics in terms of drying time, flexibility, adhesion, scratch, impact and chemical resistance. The conversion percent was not reported.

Saravari et al. synthesized water-reducible hybrids from the reaction between monoglycerides prepared from modified palm oil and carboxy-functional acrylic copolymer [84]. Modified palm oil was produced by interesterification of palm oil with tung oil whereas carboxy-functional acrylic copolymer was prepared by radical copolymerization with n-BMA and MA. All the prepared water-reducible acrylic-alkyd resins were yellowish viscous liquids. Their films were dried after adding 2 wt% of Co-Zr drier and baking at 190˚C within 90-120 min. These films showed good water, acid and alkali resistances.

Acrylate grafted dehydrated castor oil (DCO) alkyd had been synthesized by Subhasri Majumdar and co-workers by using solution method [85]. Significant improvements were observed in the properties of the DCO alkyd resin after modification with acrylate. The performance of the MMA modified alkyds has been found to be better than BMA modified alkyds. After modification with MMA, the glass transition temperature (T_g) of resin has increased, resulting in improvement of drying time and mechanical properties of the coating. In addition, MMA modified alkyds possess better weather resistance compared to n-BMA modified resins.

Modification of alkyds with styrene and other vinyl monomers has been carried out for over half a century. Styrene modified alkyds provide lower costing, better colour and faster drying time as well as water and alkali resistance properties. These modified alkyds are applied mostly in very rapid air drying and low temperature baking finishes for industrial use [86-88]. However, these modified alkyds have not been used for weatherwork paints of ships in view of poor resistance to weathering.

Styrenation of drying and semidrying oils of sunflower and linseed oils, via the macromer technique was studied by T. Akbas et al. [89]. For this purpose, the macromers of the oils were prepared by two successive steps. First, partial glycerides (PG) were prepared by glycerolysis reaction between triglyceride oil and glycerol. Subsequently, the macromer was obtained by the transesterification reaction of PGs with MMA in the presence of a catalyst. The macromers prepared were then copolymerized with styrene in the presence of benzoyl peroxide (BPO) as initiator. It was concluded that both sunflower and linseed oil-based copolymers gave satisfactory alkali resistance. The sunflower oil-based copolymers have shorter drying times than linseed oil-based copolymers. Sunflower oil-based samples had greater viscosities compared to those of linseed oil-based samples.

In another study applying same method, acrylic acid was used as the acrylic monomer [90]. It was reported that sunflower oil-based product had the shortest drying time because the sunflower oil-based polymer had higher molecular weight. The sunflower oil-based copolymer showed a larger increase in the viscosity than the linseed oil-based sample and the rate of polymerization decreased with increase in the unsaturation of the oil used. Previous reports have also shown that vinyl esters of the unsaturated fatty acids either decreased the rate or stopped the polymerization [91-93]. Sunflower oil is a semidrying oil rich in linoleic acid. Linseed oil is a drying oil rich in linolenic acid. Semidrying oil-based sample exhibited good film properties with excellent water, alkali and acid resistance, while drying oil failed due to very slow polymerization rate.

An acrylate-functionalized alkyd resin, with at least one drier, and water or organic solvent has been described in U.S. patent application Ser. No. 09/596, 269. The acrylate-functionalized alkyd resin was the reaction product of an alkyd resin and a glycidyl methacrylate. The glycidyl moiety of the glycidyl acrylate being the reactive moiety that functionalized the alkyd resin and the product consisted pendant reactive acrylate moieties.

Another method of preparation for alkyd-acrylate hybrids, beside those mentioned above is the use of free radical polymerization of acrylic monomers in the presence of an unsaturated alkyd resin using emulsion or miniemulsion technique. There are several complications and limitations reported for this kind of system, such as phase separation of alkyd and acrylate monomers as well as secondary nucleation. Tsavalas et al. reported acrylating the alkyd by miniemulsion techniques and free radical reactions between completed alkyds and acrylic monomer mixtures [77].

A stable emulsion of alkyd and acrylate monomers can be formed by using miniemulsion technique which also decreases the secondary nucleation significantly [94]. Uschanov et al. synthesized tall oil fatty acids-based alkyd resins and alkyd-acrylate copolymers by this procedure [95]. The research was focused on investigation of the influence of different acrylate and alkyd components and their ratios on the hybrid polymerization and on the binder properties. The results revealed that the polymerization rate diminished when alkyd content was increased. The overall conversion was at lower when conjugated alkyd resin was used compared to non-conjugated alkyd resin.

Acrylic dispersions and alkyd emulsions each have their own advantages and disadvantages. For example, an alkyd emulsion would be much more attractive with a harder film directly after application. Acrylic dispersions, on the other hand, have poor chemical and water resistance properties. It is believed that a very homogeneous mixture of alkyd and acrylic polymer can be a method of decreasing the negative effects of both binders [96].

In alkyd-acrylic hybrids the fast physical drying from the acrylic dispersion could be combined with the oxidative curing of the alkyd producing a binder with faster physical drying than an alkyd emulsion and a better chemical and water resistance than acrylic dispersion. A more homogeneously mixed hybrid can be prepared in a special manner: the acrylic phase can be polymerized in emulsion in the presence of colloidal alkyd droplets. Following these experiments, Nabuurs et al. prepared alkyd-acrylic hybrid systems for use as a binder in water borne paints by polymerizing acrylic monomers in the presence of colloidal alkyd droplets. Tall oil fatty acid and stearic acid were used to synthesize the alkyd with MMA, BMA and BA as acrylate monomer. The hybrid with fully saturated fatty acids reached a conversion of 100% after less than 1 h, whereas the hybrid with the highest concentration of unsaturated fatty acids reached a conversion of 93% after about 3 h [24].

Heiskanen et al. described the development of hybrid binders prepared via free radical polymerization of acrylic monomers in a presence of an unsaturated alkyd resin by emulsion polymerization technique [97]. MMA, methacrylic acid and butyl acrylate were used as monomers. Three types of alkyd emulsion formulations were used, although the emulsions were based on the same commercial tall oil isophthalic acid alkyd resin. The alkyd resin had an oil length of 80%. Hybrids with different alkyd-acrylic ratios and acrylic parts were prepared and examined. The results exhibited alkyd-acrylic hybrids with different acrylic components can be prepared with good conversion and high solid content. The highest viscosity dispersions were attained with MMA/alkyd hybrids. The results confirmed that the alkyd-acrylic hybrid had shorter drying time than a conventional alkyd emulsion.

Another technique has been considered by Shim et al. [98]. Firstly; an alkyd resin is made with an unsaturated fatty acid, phthalic anhydride (PA), tetrahydrophthalic anhydride (THPA) and trimethylolpropane. The resulting alkyd was then functionalized through the use of radical polymerization of acrylic monomer with a peroxide initiator. It was shown that the resulting coatings had excellent properties, such as pencil hardness, cross-hatch adhesion and water resistance. The films also exhibited good shelf life and corrosion resistance.

1.11 Scopes of study

The main aim of the project is to develop new copolymers with novel properties. The present project has two objectives. The first objective is to investigate the reactions of MMA with palm oleic acid-based macromers to produce copolymers with new properties, while the second objective is to characterize the new materials and investigate their application in surface coating. The methodology is briefly described as follows:

I. Incorporate unsaturated palm oleic acid in preparation of three palm oil-based macromers by varying the oleic acid content to 28, 40 and 65%.

II. Obtain the evidence of oleic acid incorporation into the macromers from the FTIR and ^{1}H-NMR spectroscopies.

III. Investigate kinetics of formation of the macromers.

IV. Study the thermal stability of macromers.

V. Use of the "macromers" to copolymerize with MMA.

VI. Synthesize three series of copolymers by using macromers that contain different oil compositions with different monomer/MMA ratio.

VII. Determine the kinetics of copolymerization reactions based on different of macromer/MMA ratio.

VIII. Characterize the molecular structures of copolymers by FTIR and ^{1}H-NMR in order to obtain evidence of C=C of the macromers that has reacted with MMA during the copolymerization reactions.

IX. Study the thermal stability of copolymers.

X. Evaluate the new materials in surface coatings.

This thesis consists of six chapters; chapter one present an introduction and background of the work. Basic chemistry, coatings, alkyd resin, raw materials used in preparation of alkyd resin and mechanism of polymerization reactions are also described. Chapter 2 provides a comprehensive description of the experimental techniques and raw materials used throughout the research. The research methodology is also outlined. The formulation of samples along with the synthesis methods used to study macromers and reaction between raw materials in the macromers preparation are presented in chapter 3. The progress of reaction in the macromers preparation, a plausible mechanism for their syntheses and the properties of macromers are investigated. The FTIR, ^{1}H-NMR and thermal analysis are used to study the macromer's reaction and structure. Kinetics of polyesterification of macromers produced are studied. Thermal decomposition analyses of three kinds of macromers are investigated. Chapter 4 deals with the reactions which have been carried out in preparation of copolymers. In this chapter, evidences on formation of copolymer (MMC) using FTIR, ^{1}H-NMR, differential scanning calorimetry (DSC) and thermal gravimetery analysis (TGA) will be provided. The loss modulus and mechanical properties of copolymers are analyzed employing dynamic mechanical analysis (DMA).

The coating characteristics of resulting copolymers are improved by butyl acrylate (BA) monomer and the reaction of BA is monitored with ^{1}H-NMR and DSC. Thermal stability and mechanical properties of resulting modified copolymers (MMBC) are examined using TGA and DMA respectively. Chapter 5 focuses on the acrylic coatings. Initially, the coating methods on the mild steel panel were investigated and testing methods of coating such as drying time, adhesion test, pencil hardness test and chemical resistance test have been described. The results have been presented and analyzed in this chapter.

The next and final chapter; Chapter 6 provides detailed discussion and the conclusions. Additionally, this chapter explores the possible future research direction on acrylic alkyd resin.