CHAPTER 1

INTRODUCTION

Rubber and palm oil are the two major agricultural crops in Malaysia. These two commodities play important roles in the country's economy, offering various job opportunities in the rubber and palm oil industry, besides helping to develop many other related industries. In recent years, there are growing interest of utilising renewable resources in production of industrial products, such as coatings, functional materials, thermoplastics and many more. In this work, palm stearin which is the by-product from fractionation of palm oil was utilised in the synthesis of alkyd resin. The resultant alkyd is not only less expensive owing to the relatively low cost of palm stearin but is also environment-friendly. Throughout the course of this study, the potential use of palm stearin based alkyd as crosslinking agent in epoxidised natural rubber with 50 mol % of epoxidation (ENR50) was investigated. Blending rubber and alkyd via solvent casting method serves as an important route for crosslink formation between suitable functional groups present in the two polymers.

1.1 Polymer blends

Polymer blending has become a very important contributor in the development of new polymer materials. This technique of joint polymerisation between two or more polymers was first introduced by Parkes (1846) through his blends of trans- and cis-1,4-polyisoprene, i.e., natural rubber, NR with gutta-percha, GP partially co-dissolved in CS_2. Blending these two isomers resulted in partially crosslinked (co-vulcanised) materials whose rigidity was controllable by altering the blend compositions and/ or adding fillers. Over the years, polymer blends continue to develop alongside with the

emerging polymers and has been one of the major area of research and development among researchers and polymer chemists today.

Polymer blend is defined as the mixture of at least two macromolecular substances, polymers, or copolymers, in which the ingredient content is above 2 wt % (Utracki, 2002). It has been estimated that polymer blends and alloys consume about 30 wt % of all manufactured polymers with about 9 % per annum growth in sales volume (Brown, 2002). The principal market for polymer blends is in the automotive industry, where plastics were used to substitute metals and homopolymers in cars. Application of these plastics frequently results in weight savings that increased fuel efficiency besides providing low temperature impact resistance and good paintability to the vehicles. Other important markets of polymer blends include the electrical and electronics components, medical devices, and exterior building and construction applications.

The advantages of polymer blending compared to development of new polymeric materials or polymerisation technology have been well-documented (Mohanty et al., 1996; Robeson, 2007). Some of the advantages include: (i) Producing materials with properties profile combinations of the blended polymers at reduced cost. (ii) Improvement of specific properties and extending the performance of engineering resins. (iii) Providing ways of scrap reduction as blending technology makes it possible to produce high performance articles via recycling industrial and/ or municipal plastic waste. (iv) Higher rate of production as blending ascertain quick formulation changes and improves product uniformity.

1.1.1 Preparation of polymer blends

In general, the words mixing, blending and compounding share a similar meaning where they indicate an action of combining ingredients into one mass, so that the constituent parts are indistinguishable. However, in the plastic processing, each of the terms has different definition. Mixing indicates the physical act of homogenisation (e.g., mixing of fractions), blending usually indicates preparation of polymer blends or alloys, while compounding indicates incorporation of additives into a polymeric matrix, viz. antioxidants, lubricants, pigments, fillers, or reinforcements (Utracki & Shi, 2002). In the laboratory as well as on plant scale, polymer blends can be prepared through different techniques such as solution blending, latex blending, melt mixing, freeze drying, etc.

(a) Solution blending

In this process, polymer pairs are dissolved in common solvent before being blended together. Thin solid film of the blend is subsequently obtained either through evaporation of solvent or precipitation of the polymer mixture by addition of precipitating agent. An important criterion that should be considered in this blending is the selection of suitable solvent which is mutually exclusive for the blend components. Different solvent may have different interaction with the constituent homopolymer, which may also vary the mechanical and morphological properties of polymer blends. Low boiling solvent is usually preferred due to its high diffusivity, while high boiling solvent may be suitable for polymer pairs exhibiting high T_g.

Blending of polymers using this technique provides several advantages (Ricklin, 1983) which include:

- higher quality (uniformity) and thinner film
- freedom from pinholes and gel marks
- purity and clarity
- lack of residual stresses
- possible to produce patterns or dull finishes

However, the solvent used in this method can give rise to certain problems (George & Thomas, 2011). Firstly, it is difficult to find a common solvent where both the polymer pairs are readily soluble. Problem also arises during the removal of solvent to obtain thin film of the blend where phase separation could possibly happen as a result of the increase in the concentration of polymer during evaporation of solvent. Besides, incomplete removal of solvent may affect the results of analysis on the blend.

(b) Latex blending

Latex blending is the preferred technique when the polymers to be mixed are in aqueous latex form. The blend is prepared via blending two or more polymer lattices under controlled mixing speed and pH, and subsequently spray-dried or coagulated to obtain a homogeneous and non-segregated solid latex blend. Some early examples of latex blending include the blending of rubber lattices (natural or synthetic), e.g. NR latex and acrylonitrile-butadiene rubber (NBR) latex blends (Chowdhury, 2007), and blending of rubber lattices with thermoplastic acrylates, methacrylates and vinyls, e.g. latex blends of NR and poly(methyl methacrylate) (PMMA) (Ho et al., 2001).

The particle size of the phases prepared via this technique can be controlled by emulsion polymerisation. Broad spectrum of particle size ranging from fine dispersion (drop diameter, d= 100 to 200 nm) of homo- or co-polymer to alternatively large drop aggregates can be produced via latex blending. Besides, the rubber phase can be partially crosslinked during polymerisation. However, this technique is not highly practical as the resultant latex blend contain high amount of contaminants, emulsifiers, residuals of the initiators, chain transfers, stabilisers, etc (Utracki & Shi, 2002).

(c) Melt mixing

Melt mixing process is the simplest techniques in polymer blending where polymers are blended in the melt state using suitable devices like rollers, extruders or kneading machines. This mechano-chemical blending technique is widely used for the blending of elastomer-plastic blends and plastic-plastic blends where high shearing forces is necessary for the mechanical blending of high molecular weight elastomer. The extent of intermixing of polymer blend is dependent on the diffusion or mobility of the macromolecules inside the highly viscous melt. Under suitable reaction conditions, the polymer melts can undergo chemical reactions such as transesterification, transamidation, crosslinking, and chain scission resulting in the formation of block or graft copolymers which enhance the interphase adhesion between the polymer components (Braun et al., 2000).

(d) Freeze drying

This method is useful when preparing blend from two thermodynamically immiscible polymer pairs. In this process, a single phase solution containing the blend components was quenched down to very low temperature and the solvent is frozen by freeze-drying method. This way the frozen polymers mixture will preserved the same state as that of the dilute solution where the immiscible polymers were dispersed randomly in the regions throughout the frozen solvent and have very little chance to segregate (phase separate). Solvent can then be removed by sublimation without affecting the phase morphology of the mixture. To a large extent, therefore, the resulting blend will be independent of the solvent, if the solution is single phase before freezing and the freezing occurs rapidly (Shaw, 1985).

1.1.2 Miscibility of polymer blends

From thermodynamic point of view, polymer blends can be categorised into two groups i.e. miscible and immiscible. When two macromolecules are blended together, they will either mix homogeneously or separate into two phases. In most cases, the polymer pairs are immiscible with one another. These polymer blends often consist of a dispersed phase in the form of more or less regularly shaped particles in a continuous matrix. It is necessary to devise compatibilisation strategies to stabilise the blend morphology in order to provide optimum properties and good physical performance. If the blend is not compatibilised, there is high chance that the dispersed phase will coalesce when subjected to high heat and stress treatment, leading to gross phase segregation in the blend.

Miscibility of polymer blends is dependent on the Gibbs free energy, ΔG during the mixing process. The most important relationship (Utracki, 2002; Robeson, 2007) governing the mixtures of dissimilar components 1 and 2 is:

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (Eqn. 1.1)$$

where ΔG_m is the free energy of mixing, ΔH_m is the enthalpy of mixing (heat of mixing) and ΔS_m is the entropy of mixing. A polymer blend is miscible, homogeneous down to the molecular level when the blend satisfied two basic requirements for miscibility where the ΔG_m is smaller than 0 ($\Delta G_m < 0$) and having a positive value of the second derivative of ΔG_m: $\delta^2 \Delta G_m / \delta\phi^2 > 0$.

When mixing two low molecular weight substances, the entropic effect is overwhelming as the degree of disorder is high after mixing, thus driving ΔG_m to be more negative. However, in a polymeric system, it is seldom for $\Delta G_m < 0$ as the $T\Delta S_m$ term is very small. Although ΔS_m is positive when mixing or blending polymers, the increase is however not as great as compared to mixing low molecular weight liquids. This is due to the massive size of the polymer itself and intermolecular forces within the chains, causing mobility of the polymer chains to be substantially restricted. Therefore, miscibility is dominated by the ΔH_m value which relies on intermolecular forces between the components of the polymers and will create a favourable situation when the strength of interactions between the two polymer chains is very high (Peacock & Calhoun, 2006). In some of the cases, copolymers were used to substitute homopolymers to create strong interactions between polymer components, thereby promoting miscibility.

1.1.3 Properties of blends

Blending of two or more polymers is usually driven by the aim to achieve blend with properties combination from each polymer. However, the behaviours of polymers in a blend may not necessarily be the same as expected from the behaviours exhibited by them as an individual component. Some of the factors which govern the behavioural pattern of polyblends (Ghosh, 2008) include:

(i) Extent of phase separation

(ii) Nature of the phase provided the matrix material

(iii) Character of the dispersed phase

(iv) Interaction between the two component polymers, etc.

Figure 1.1 shows the idealised behavioural patterns from blending two or more polymers that are miscible and immiscible (Brown, 2002). In the case of miscible polymer blends, the polymer pairs are intimately mixed. The strong interactions between the polymers have resulted in a blend with intermediate physical properties between those of the individual polymers depending upon the proportion of each polymer present. In a common example, miscible blend will exhibit a single T_g which vary linearly with the blend compositions. For immiscible blends, there are insufficient interfacial adhesion and/ or high interfacial tension between the two polymer phases. Such blends generally exhibit physical properties worse than those of either individual polymer. However, when the immiscible blends are compatibilised either through reactive compatibilisation or addition of separate material that act as compatibilsing agent, one may expect a synergistic combination of properties from each polymer.

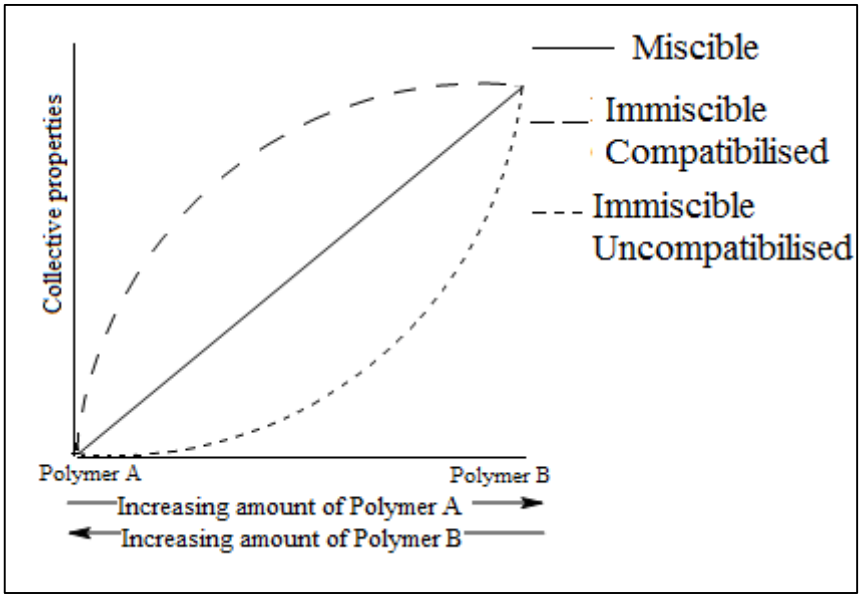


Figure 1.1: Idealised behavioural patterns of polymer blend as blend composition changes (Brown, 2002).

1.1.4 Commercial polymer blends

Commercially available polyblends are generally classified into three types: (i) Elastomer-elastomer blends, (ii) Plastomer-plastomer blends, and (iii) Elastomer-plastomer blends. Elastomers are widely blended with different elastomers due to the fact that a single elastomer usually fails to offers favorable properties and overall cost advantage. NR is blended with synthetic rubber with the purpose to improve a wide range of properties such as tack, resilience, tear strength, heat build-up as well as fatigue resistance. Sometimes, selected synthetic rubbers are blended with different synthetic rubbers or with primarily NR based compound. A common example of elastomeric blend can be found in automotive tire, which majorly comprised of blend of two or more rubbers from NR; styrene butadiene rubber, SBR; synthetic polyisoprene rubber, IR; polybutadiene rubber, BR; butyl rubber, IIR and ethylene propylene rubber, EPDM or EPM (Datta, 2005).

In plastomer-plastomer blends, selection of thermoplastic polymers for combination is important to achieve blends or alloys with synergistic properties at reduced price. Thermoplastic polymers can be classified into four families ranging from commodity, transitional, engineering and performance thermoplastics (Kienzle, 1988), as shown in Figure 1.2. By blending polymers from two different families, the property of an expensive polymer may be partially exploited, using less costly polymer to provide specific property advantage while reducing overall compound cost. An example of such blend is that of acrylonitrile butadiene styrene, ABS and polycarbonate (Muccio, 1991). Polycarbonate is naturally flame retardant and famous for its high impact resistance but it has a disadvantage of being relatively expensive. Polyblend based on ABS and polycarbonate combines excellent heat resistance, high impact strength and flame retardance characteristics besides offering the cost advantage over the use of only polycarbonate.

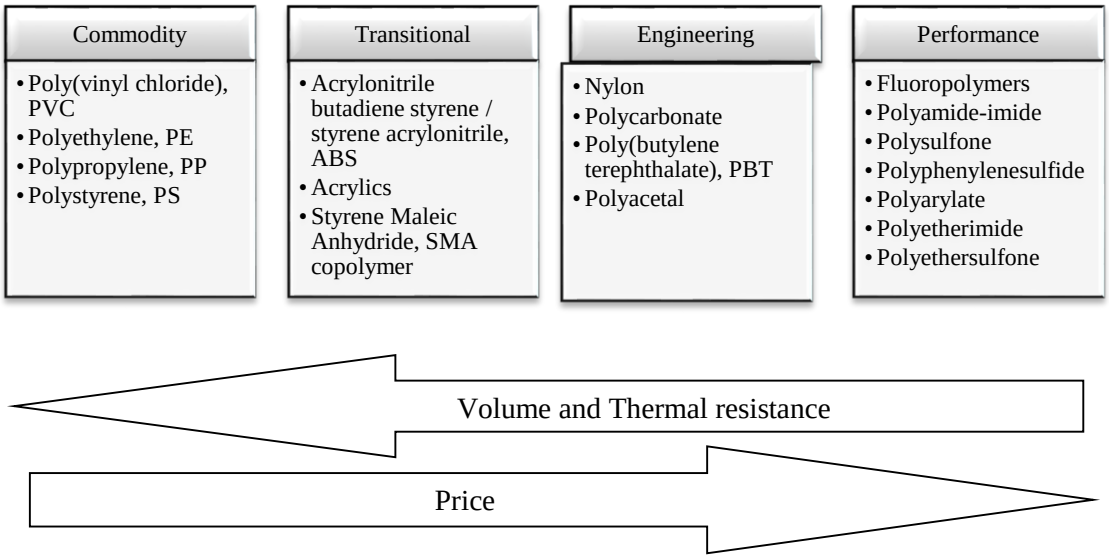


Figure 1.2: Classification of thermoplastic polymers

The combination of plastomers and elastomers or better known as thermoplastic elastomers, TPE represents another group of commercial polyblends, which combine the processability of thermoplastics and functional performance of elastomers. The ability of TPE to become fluid on heating and then solidify on cooling gives manufacturers the ability to produce rubber-like articles using the conventional plastics equipment, such as injection moulders, blow moulders and extruders (De & Antony, 2001). Such unique behaviour of TPE is mainly associated to its structure which contains both hard glassy domains of low extensibility and high crystalline melting point, T_m and soft rubbery segments of very low T_g. The hard segments are responsible for the mechanical strength, heat resistance and swelling behaviour, while the nature of the soft rubbery segments determines the elasticity and low temperature flexilibity of the blends. A commercial example of TPE is the blend of EPDM with polypropylene (PP) which is used for bumper covers and automotive fascia.

1.1.5 Self-crosslinking polymer blends

Self-crosslinking or self-vulcanising polymer blends form a novel family of polymer blends. They are physical mixtures of two or more polymers, which capable of undergoing crosslinking reaction upon exposure to high temperatures without the aid of external crosslinking agents (Antony et al., 2001). When one of the blend components is a rubber, they are termed as “self-crosslinking rubber blends”, and it could either be a rubber/rubber or rubber/thermoplastic blend. Generally, self-crosslinking blends are generated through blending of two polymers having suitable chemical functionalities. When temperature of the system is raised, the two polymers form crosslink networks via chemical interaction between functional groups in the base polymers. Some examples of self crosslinking rubber/rubber blends include the binary blends of

ENR/Chlorosulphonated polyethylene rubber (CSM) (Mukhopadhyay et al., 1990a; 1990b); ENR/Carboxylated nitrile butadiene rubber (XNBR) (Alex et al., 1989; 1990a; 1990b); ENR/Polychloroprene (CR) (Alex et al., 1991a); ENR/Zinc salt sulphonated EPDM rubber (Zn-SEPDM) (Manoj et al., 1993; 1994); CSM/XNBR (Mukhopadhyay et al., 1991a) and CR/XNBR (Mukhopadhyay et al., 1991b; 1992). Ternary rubber/rubber blends such as CR/XNBR/ENR (Alex et al., 1991b) and CSM/XNBR/ENR (Roychoudhury et al., 1992) blends have also been reported to be self-crosslinkable. Typical self-crosslinking rubber/thermoplastic blends include the binary blends of PVC/XNBR (Ramesh & De, 1990), PVC/ENR (Ramesh & De, 1991; 1993a), PVC/NBR (Ghosh et al., 1992; Sen & Mukherjee, 1993) CR/Poly(acrylic acid) (PAA) (Ramesh & De, 1992); and PAA/ENR (Mallick et al., 1993) and a ternary blend of PVC/ENR/XNBR (Ramesh & De, 1993b).

1.2 Epoxidised Natural Rubber (ENR)

1.2.1 Background

ENR is a semi-synthetic rubber which has high commercial value due to its highly polar structure (Figure 1.3) as compared to NR. Chemical modification on NR via epoxidation was discovered as early as in 1922 when Pummer and Burkard treated NR with peroxyacid. Since then, various preparation methods and reaction conditions in the synthesis of ENR were reported and the products were variously described as hard thermoplastic (Bloomfield & Farmer, 1934; Ng & Gan, 1981) to soft rubbery polymers (Burfield et al., 1984a). In Malaysia, ENR was first commercialised by Kumpulan Guthrie Berhad, with the brand name of Dynaprene which is now known as Epoxyprene 25 and Epoxyprene 50, where the numbers indicate the mole % of epoxide groups.

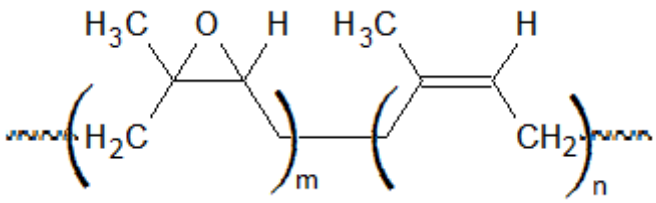


Figure 1.3: General structure of ENR

1.2.2 Preparation of ENR

Epoxidation of NR in solution or at latex stage involves the formation of oxirane (epoxide) rings in the main chain of NR. The epoxidising agent used in this modification is usually a peroxycarboxylic acid which generated through in situ reaction between hydrogen peroxide and a water soluble carboxylic acid. An example of the reagent pairs involved in the epoxidation of NR is hydrogen peroxide and formic acid. In situ reaction between the reagents generates the peroxoformic acid and a water

molecule. Note that the reaction is a reversible reaction where the peroxoformic acid will decomposes back to formic acid when an oxygen atom is generated at the unsaturation sites of NR. Formic acid can be viewed as a catalyst in the epoxidation reaction.

$$\mathrm{HCOOH} + \mathrm{H_2O_2} \rightleftharpoons \mathrm{HCO-OOH} + \mathrm{H_2O}$$

Epoxidation of NR is an uncontrollable reaction which often favours the formation of secondary products resulted from the ring opening reaction of the epoxide group. This could possibly due to the fact that the 3-membered oxirane ring is highly strained and will tends to ring open to release its strain (Niranjan, 2009). The type of secondary ring-opened products formed may vary depending on the level of epoxidation in the rubber. At low level of modification, majority of the epoxide groups are isolated in the rubber chain, hence the ring-opened products are normally the *trans* diol (Gelling, 1991). Conversely, at high modification, the number of adjacent epoxide groups increases, five-membered cyclic ether becomes the major product (Gelling, 1985). Under carefully controlled conditions, such as maintaining low pH and moderate reaction temperature (50-70 °C) for epoxidation, NR latex can be epoxidised up to 75 mole % without formation of secondary ring opened products. Additional step such as neutralising the residual acidity from the ENR synthesis via addition of base such as anhydrous calcium carbonate, magnesium oxide, calcium oxide and calcium stearate followed by washing well with water may also help in minimising the formation of secondary products.

1.2.3 Properties of ENR

Since ENR retains the *cis* structure stereoregularity and intermolecular attractions of NR, it tends to behave like NR where it is capable of strain crystallisation up to 50 mol % of epoxidation. Nevertheless, majority of the properties in the rubber have been altered after introduction of oxirane groups in NR backbone and these properties are observed to change systematically with the level of epoxidation. As a result of the epoxidation, polarity of the rubber increases thus enhances its resistance towards oils and impermeability towards gas. T_g of the rubber also increases with the rising level of epoxidation due to reduction in chain flexibility. In the mechanical aspects, ENR has good abrasion resistance; high wet grip and good damping properties, but the modulus, hardness, tensile strength, elongation at break of ENR50 compounds are comparable to corresponding NR compounds. Epoxidation also means that there is reduction in the unsaturation level in the rubber which may be good for the ozone resistance characteristic in raw ENR as compared to raw NR. However, it is unfavourable for ENR vulcanisates, as they are more prone to ageing than comparable NR vulcanisates (Brydson, 1994), owing to the low unsaturation level in the rubber.

1.2.4 Applications

Although ENR exhibits superior properties compared to most commercially available rubber, it is only suggested to have a wide range of potential applications rather than established uses. Patents have been filed on the adhesive and sealant properties of ENR which can be developed for binding vulcanised rubber of different polarity and rubber compounds to steel, for use in the area of epoxy resin technology and to develop glazing sealing systems (Brydson, 1994). Tire industry offers the largest potential market for ENR due to the excellent mechanical properties the rubber has to

offer, making it attractive for the production of tire treads, inner liners and tubes. ENR 25 filled with silica is suitable for tire treads making due to its high wet traction and good fuel economy from low rolling resistance.

In addition, partial substitution of carbon black filler to silica is easy with ENR due to the high reinforcement achieved without the need to resort to silane coupling agents hence further enhances the fuel economy. ENR50 has been utilised as a replacement for butyl rubbers in the making of tire liners and tubes due to its low air permeability property. Tires with inner liners based on the ENR/NR blends have been manufactured in Malaysia and was confirmed to have good air retention properties compared to the standard chlorobutyl/NR liner compound. However, ENR-based inner liners possess a disadvantage of having high rate of water vapour permeation. On the other hand, ENR is utilised in the making of general rubber goods due to its high wet grip properties such as in the making of shoe soles and non-slip flooring mat. ENR is also used in the construction of conveyor belts due to its adhesive properties and the combination of high strength and low resilience of ENR based conveyor belts are advantageous under severe service conditions.

1.2.5 Vulcanisation and Crosslinking in ENR

Vulcanisation generally applied to rubbery or elastomeric materials where crosslinks are inserted between polymer chains through the use of vulcanising agents. The crosslink may be a group of sulfur atoms in a short chain, a single sulfur atom, a carbon to carbon bond, a polyvalent organic radical, an ionic cluster, or a polyvalent metal ion (Coran, 2005).

As ENR exhibits C=C groups like NR, it can be cured by sulphur or peroxides formulations in the presence of accelerator. In addition, ENR may be cured through the crosslinking of the epoxide groups with other functional chemicals such as amine compounds and dicarboxylic acid systems.

(a) Sulfur vulcanisation

Sulfur vulcanisation method was first introduced in the year 1841 by Charles Goodyear where NR was vulcanised by heating with 8 phr of elemental sulfur at 140 °C for 5 hours. However, this conventional method is not highly practiced as it requires long hours of vulcanisation and was eventually replaced by accelerated sulfur vulcanisation method in which organic chemical accelerators were used in addition to the sulfur formulations. There are three types of accelerated sulfur vulcanisation systems, namely:

1) Conventional systems (CV) containing high sulfur/accelerator ratio
2) Efficient systems (EV) containing high accelerator/sulfur ratio
3) Semi-efficient systems (Semi-EV) containing sulfur/accelerator ratio which intermediate to CV and EV

The formulations for accelerated sulfur vulcanisation of ENR are shown in Table 1.1.

Table 1.1: Formulations for accelerated sulfur vulcanisation of ENR (Gelling, 1991)

Compound	CV	Semi-EV	EV
Polymer	100	100	100
Filler	Varies	Varies	Varies
Process oil	Varies	Varies	Varies
Calcium stearate	5	5	5
Zinc oxide	5	5	5
Stearic acid	2	2	2
Antioxidant[a]	2	2	2
Antioxidant[b]	1.5	1.5	1.5
Paraffinic wax	3	3	3
Sulfur	2.5	1.5	0.5
CBS[c]	0.6	-	2.5
MBS[d]	-	1.5	-
TMTM[e]	-	1.5	-

[a]N(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine

[b]Poly-2,2,4-trimethyl-1,2-dihydroquinoline

[c]N-cyclohexylbenzothiazole-2-sulphenamide

[d]2-morpholinothiobenzothiazole-2-sulphenamide

[e]Tetramethylthiuram monosulphide

In the work of Gelling and Morrison (1985), it was reported that ENR50 cured faster and more efficient compared to NR via the unaccelerated sulfur vulcanisation. The higher sulfur crosslinking rate in ENR50 is associated to two factors. First, the randomly epoxidised ENR having isolated double bonds in its rubber chain inhibits the formation of intramolecular sulfide links, the side reaction between chain propagating

species with neighboring double bond. Second, it is presumed that the epoxy groups acts as activator to the adjacent double bonds.

However, CV is not recommended to cure ENR due to the poor ageing properties shown by its vulcanisate. The oxidation of sulphides will results in the formation of sulphenic acids which catalyses the ring-opening of the epoxide groups. The formation of the ether crosslinks will then results in the hardening of the vulcanisate. Therefore, Semi-EV and EV are the more suitable methods to cure ENR and the resultant ENR vulcanisate is expected to exhibits comparable properties to those of NR but with inferior ageing resistance. To optimise the ageing resistance of ENR, it is essential to maintain the vulcanisate at basic condition via addition of base such as calcium stearate.

(b) Crosslinking involving epoxide groups of ENR

ENR shows unique vulcanisation characteristic where it is capable to vulcanise through crosslinking reaction involving epoxide groups. The high amount of strain present in the 3-membered epoxide ring causes the oxirane group to be susceptible to nucleophilic addition reaction when assisted by either an acid or base catalyst. This will result in the attachment of nucleophile bearing molecule to the macromolecular chain of ENR by various types of linkages. Usually, the crosslinking agent exhibits di- or multifunctionality which is capable to react with more than one epoxide groups from different ENR molecules to form effective crosslinking.

1.3 Alkyd

1.3.1 Background

Alkyd resins are polyesterification products generated from the reaction between polyhydric alcohols and polybasic acids in the presence of monoacids as major part of its composition. The term 'ALKYD' was introduced by Kienle in 1927 where 'AL' comes from the word alcohol while 'KYD' corresponds to the 'cid' in acids (Paul, 1986). Alkyds are categorised as B-stage resins, having far lower molecular weight compared to thermoplastic polymers and containing higher amount of functional groups, such as hydroxyl groups, carboxyl groups and C=C bonds (Manea, 2008).

The development of alkyd resins started in 1847 with the production of polyester coatings by Belzelius who conducted polycondensation of dicarboxylic acid with polyol (eg. glycerol) to form glyceryl polytartrate. This was then followed by Smith, in 1901, who prepared glycerol polyphthalate. However, the reaction products were described as hard, brittle and have no commercial significances. It was until 1914, when Kienle incorporated natural oil fatty acids into polyester, the product became a solvent soluble film-forming resin which capable of being air-dried. Alkyd was then known as oil-modified polyester which commonly formed from the polycondensation of phthalic anhydride (PA) with glycerin and monobasic fatty acids. The discovery of transesterification process of oils, in 1927, develops an economical way for the production of alkyd resins where oils can be directly used as the basic components in alkyd synthesis.

Alkyd resins are the predominant synthetic resin used in the paint and surface coating industries. The several reasons to the great demands of alkyds resins would be due to the low production cost, long shelf life and the versatile nature of alkyd which could be modified to provide products fit for a very wide range of substrates. In

addition, alkyds exhibit excellent properties such as rapid drying, good pigment wetting, adhesion for multiple substrates and attractive flowability which ease the application of paints. Nevertheless, alkyd resins, being modified polyesters, show poor chemical resistance particularly to alkalis as they are susceptible to ester hydrolysis.

1.3.2 Alkyd Raw Materials

The diversity of alkyds available today could be due to the wide variety of possible reactants that can be used in the alkyd synthesis. Generally, preparation of alkyd resins requires at least three basic components which include fatty acids or oils, polyalcohol and dicarboxylic acids or their anhydrides. The selection of specific components in specific amounts enables the alkyd to be prepared to the desired properties and applications.

(a) Oils and fatty acids

Oils and fatty acids are the predominant renewable raw materials in alkyd resin which influence the alkyd properties in terms of drying time and discoloration (Manea, 2008). Oils may be derived from vegetable or animal sources and are chemically composed of triglycerides or known as glycerol ester (glycerine). When the oil is treated with a strong base, followed by acidification, the triglycerides are converted into fatty acids and glycerol. This process is known as saponification where the base functions to cleave the ester bond in the triglycerides. There are 2 types of triglycerides, (i) simple triglycerides which composed of three identical fatty acids attached to the glycerol structure and (ii) mixed triglycerides which made up of different fatty acids.

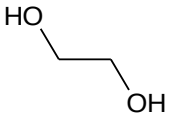
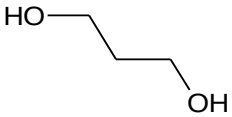
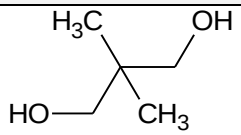
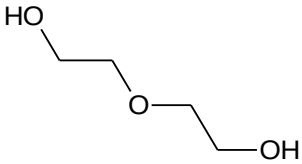
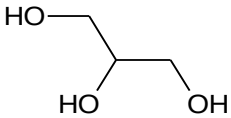
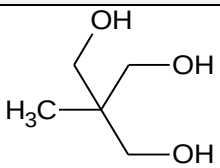
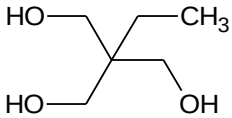
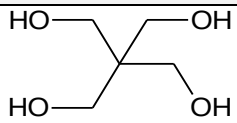
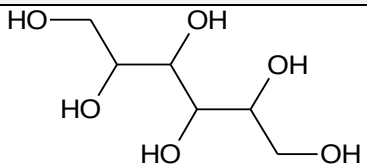
Oils are classified into three types i.e. drying, semi-drying and non-drying. The classification is based on the percentage of unsaturated fatty acids that made up the oils. Drying oils such as tung oil and linseed oil contain high percentage of fatty acids with two or more double bonds and high iodine value while non-drying oils such as groundnut oil, coconut oil and palm kernel oil have low unsaturation and mainly used for production of alkyd resins for stoving enamels. Semi-drying oils such as sesame oil and cottonseed oil are intermediate between the drying and non-drying oils and used to produce air-dried alkyds with better resistance to yellowing.

Generally, the influences of modifying oils on alkyd properties depend greatly on the nature of oil and fatty acids composition in the oil. The higher the unsaturation of fatty acids in the oils, the shorter the time needed to air-dry the resin. However, the resultant alkyd resin is prone to discolouration and has poor weather resistance. Conversely, when oil with low unsaturation is used, the resin requires longer drying time but exhibits better colour stability, weather resistance and gloss resistance (Stoye, 1996).

(b) Polyols

Broad selections of polyols are available for alkyd resins synthesis, ranging from diols, triols, tetrols, hexols, functional polyols to polyol with mixed functionality/hydroxyl-acids. Table 1.2 shows some common polyols used for alkyd synthesis along with their molecular structures.

Table 1.2: Some common polyalcohols used in alkyd synthesis

Diols		
 Ethylene glycol	 1,3-propanediol	 Neopentylglycol
 Diethylene glycol		
Triols		
 Glycerol	 Trimethylolethane	 Treimethylolpropane
Tetrols	**Hexols**	
 Pentaerythritol	 Sorbitol	

Glycerol is the most commonly used polyol, by tradition, owing to its trifunctionality. Unlike other polyols, glycerol contains 2 primary or α-hydroxyl groups and a secondary or β-hydroxyl group which exhibit different reactivity towards esterification. With the secondary hydroxyl group being less reactive than the primary one towards dibasic acid, an alkyd resin which made up of glycerol and a dibasic acid such as PA will yield a linear polyester chain with little branching (Goldsmith, 1948).

Glycerol can be converted to side product (acrolein) when it is heated at a temperature between 260 °C and 290 °C in the monoglyceride phase (Deligny & Tuck, 2000). This will then results in loss of glycerol available for transesterification reaction.

In addition to glycerol, pentaerythritol, frequently termed PENTA, is commonly employed in alkyd formulation. It has several advantages over glycerol; (i) Pentaerythritol is tetrafunctional as opposed to glycerol which is trifunctional, allowing greater amount of oils to be incorporated in the alkyd synthesis. The resultant alkyds, ranges from medium-long to extra long oil length alkyds, are not only better in film flexibility but also more economical as oil is less expensive than either glycerol or pentaerythritol. (ii) Alkyd paints made with pentaerythritol exhibit water resistance which is far more superior to that of glycerol alkyd. (iii) It offers better gloss and gloss retention. (Standeven, 2007)

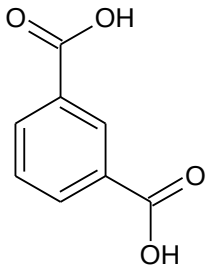
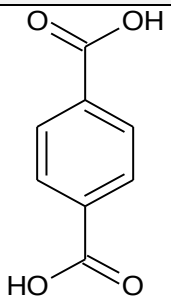
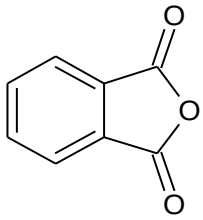
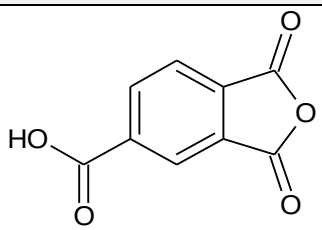
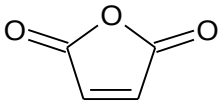
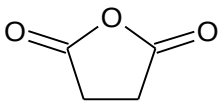
(c) Polyacids

Some examples of polyacids used in alkyd formulations are given in Table 1.3. Usually, the types of polybasic acids used are dibasic acids (aromatic and aliphatic) and its anhydrides. The ratio of aromatic or cyclo-aliphatic polyacid components in alkyd formulation may affect the hardness of the final product. Aromatic polyacids provides rigid linkages with properties of hardness and stiffness. Conversely, formulation with high aliphatic diacids leads to alkyd resins which are more flexible and elastic (Nordstrom, 2003).

PA is the most commonly used anhydride in the alkyd resin industry. It is derived from *o*-xylene and is more reactive compared to its acid derivative (orthophthalic acid) as the ring strain in the anhydrides promotes ring-opening, thus esterification with the polyol. In addition, PA offers advantages to the alkyd

manufacturers as it is easily available at a lower cost and it provides the hardness and chemical resistance in alkyd resins due to its phenyl group's resistance to rotation.

Table 1.3: Some common dicarboxylic acids and anhydrides used in alkyd synthesis

Aromatic dicarboxylic acids		Aliphatic dicarboxylic acids	
 Isophthalic acid (IPA)	 Terephthalic acid (TPA)	$HOOC-(CH_2)_2-COOH$	Succinic acid
		$HOOC-(CH_2)_4-COOH$	Adipic acid
		$HOOC-(CH_2)_7-COOH$	Azelaic acid
		$HOOC-(CH_2)_8-COOH$	Sebacic acid
Anhydrides			
 Phthalic anhydride (PA)	 Trimellitic anhydride (TMA)	 Maleic anhydride (MA)	 Succinic anhydride (SA)

Although PA is widely used for producing alkyd resins, the isomers of orthophthalic acid, isophthalic acid (IPA) and terephthalic acid (TPA) are also used but to a lower extent. Both these isomers are important to improve the drying and hydrolytic-stability in alkyd resins. Alkyd resins based on IPA have good mechanical strength as well as resistance to weathering which made them suitable as exterior wood paints, while TPA-based alkyd resins are used as electrical insulating lacquers and wire

enamels on the basis of their good heat resistance. However, both of these dibasic acids have very high melting points which render them difficult to use and leads to longer reaction times during alkyd manufacture.

MA is used in small quantities in addition to other dibasic acid (usually PA) in alkyd synthesis. Normally, the concentration of MA in alkyd formulation is restricted to 1-10 % of the PA content (Taylor & Marks, 1972). Excessive amount of MA could lead to alkyd gelation as the C=C in MA could participate in unwanted crosslinking during the synthesis. The significances of incorporation of MA can be seen from the increase in hardness and improvement in colour of the alkyd resins. The increase in the amount of unsaturation from incorporation of MA also improves the drying properties of the alkyds.

1.3.3 Preparation of alkyd

Alkyd resins can be processed via three different chemical routes, namely, the monoglyceride process, fatty acid process and acidolysis process. Each of the processes is applied based on the type of raw materials used. When oil is present as such, the procedure for manufacturing of alkyds will be initiated with the generation of difunctional moieties. Otherwise the process, when starting from acids and polyols is referred as polyesterification process (Manea, 2008).

(a) Monoglyceride process

In the preparation of alkyd where oil is used as the feedstock, it is necessary to carry out the synthesis in two stages due to incompatibility between different raw materials particularly with the oil (Deligny & Tuck, 2000). The first stage of the

synthesis, namely alcoholysis process, involved the formation of monoglyceride structure through reaction between the oil and polyol. This step is crucial to convert the insoluble polyol and glyceride phases into a single homogeneous monoglyceride phase and the monoglyceride in turn acts as solvent for the reaction with PA in the next step, esterification of the monoglyceride with diacid to form the alkyd (Patton, 1962).

In the alcoholysis stage, oil is heated with part of the polyol at 240-270 °C for 2 to 4 hours in the presence of catalyst, generally hydroxide of alkaline metal such as NaOH, KOH and LiOH. The process is carried out under inert atmosphere such as in N_2 or CO_2 to reduce discoloration and dimerisation of drying oils. Completion of the process is monitored by checking the solubility of the mixture in alcohol (eg. methanol or ethanol). Sufficient transesterification of the oil will result in the solubility of the polyol and mixture of glycerides in alcohol.

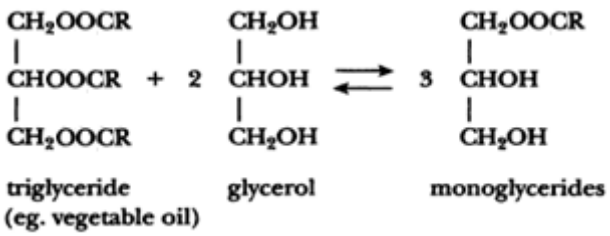


Figure 1.4: Formation of monoglyceride

Figure 1.4 shows the idealised reaction route for alcoholysis step where all the triglyceride (oil) is converted to monoglyceride when reacted with glycerol (Elliot, 1993). Practically, the products obtained from this reaction is an equilibrium mixture containing triglycerides, diglycerides, monoglycerides and glycerine, in which α-monoglyceride is the major component in the alcoholysis products. In general, the composition of monoglyceride formed is not more than 40 %, irrespective of the reaction conditions, but this proportion is sufficient to homogenise the reaction medium and allow the process to proceed to esterification step.

In the second stage, esterification takes place between the alcoholysis products and diacid to complete the alkyd reaction. The reaction temperature is maintained between 200 °C and 240 °C and completion of the reaction is monitored by checking the acid value and the viscosity of the reaction mixture.

(b) Fatty acid process

Alkyd is synthesised via fatty acid process when fatty acid is present as the major component in the alkyd composition. This process is performed in a single step where all the raw materials are charged into the reactor and heated to temperature between 190 °C and 240 °C under inert gas atmosphere. In this esterification process, all the acid components will directly compete to react with the polyols. Since the carboxyl groups of PA react faster with the primary hydroxyl groups from glycerol than those of fatty acids, the dibasic acid and glycerol form the polyester backbone structure of the alkyd while the fatty acids are the pendant moieties.

(c) Acidolysis process

Acidolysis process is a two-step process which is used when the dibasic acid is insoluble in the reaction mixture or when it has a high melting point, such as IPA and TPA (Manea,2008). The first step in this process involved heating the dibasic acid with oil at temperature between 270 °C and 290 °C until a perfect compatibility is attained. A tin or titanium catalyst may be used to speed up this process. The yields from this reaction are free fatty acids and new moieties having acid functionality generated from dibasic acids (Manea, 2008). These acids will then further react with polyol in the second step of this process.

1.3.4 Alkyd polyesterification process

The alkyd polyesterification stage, regardless of the monoglyceride, fatty acid or acidolysis method is performed either by fusion or azeotropic (solvent) process (Deligny & Tuck, 2000; Elliot, 1993). Both of these processes possess their own advantages and disadvantages as summarised in Table 1.4

Table 1.4: Alkyd resin polyesterification process

	Fusion process	Azeotropic process
Process Condition	All the raw materials are charged into the reaction vessel and reaction is carried out under inert gas atmosphere such as dry nitrogen or carbon dioxide.	An azeotropic solvent (xylene, white spirit) at an amount of 3 to 8 % is used to aid the removal of water given off by the esterification process. The reflux solvent and water liquefy when reach the condenser, placed on top of the reaction vessel and will be collected in the Dean and Stark receiver as two separate layers. Water is removed and the solvent is returned to the reaction vessel
Advantages	• Simple equipment set-up needed, leads to low production cost	• Minimal loss of components as the solvent cleans the reaction vessel walls and recycles the products which have sublimed and crystallised
Disadvantages	• Loss of components such as sublimation of PA which leads to poor reproducibility problems and increase in viscosity of the reaction mixture • Darkening of the resins	• Requires complex condensation and separation equipment, leads to high production cost • Presence of solvent reduces the viscosity of reactants which reduces the rate of reaction • Removal of solvent is necessary when preparation of alkyd which is not diluted by the azeotropic solvent is desirable

1.3.5 Classification of Alkyds

A simple way of classifying alkyds is by grouping them according to their drying properties, oxidising or nonoxidising types (Wicks et al., 2007). Other way of classification may be based on the oil length present in the alkyds where they are grouped as long oil, medium oil and short oil alkyds (Muller & Poth, 2006).

(a) Drying properties of alkyd resins

The term oxidising and non-oxidising in alkyd resins are related to the drying properties of the oil components used in the synthesis of alkyd. An oxidising alkyd is usually composed of drying or semi-drying oil fatty acids where it is capable to self-oxidise in the presence of atmospheric oxygen while non-oxidising alkyd is modified with oils containing high saturated fatty acids (non-drying oil) and hence resist oxidation. The difference in the drying ability of the alkyd could influence the physical appearance and hence potential application of the coating formed. A non-oxidising alkyd is used as polymeric plasticisers or as hydroxy-functional resins which crosslinked with melamine-formaldehyde (MF) or urea-formaldehyde (UF) resins. On the other hand, oxidising alkyd readily forms a non-tacky film by oxidative polymerisation and is used for architectural enamels, house paints, baking and air-drying undercoats.

(b) Oil length of alkyd resins

Oil length is the most practical method used to classify alkyd resins into different groups and it is defined as the percentage of oil present in the resin expressed as triglyceride. The oil length of an alkyd is calculated by dividing the amount of “oil”

in the final alkyd with the total weight of all ingredients used after subtracting the weight of water evolved from the reaction (Eqn. 1.2), expressed as percentage (Wicks et al., 2007; Kroschwitz & Hoboken, 2003). In the case where fatty acids were used in the alkyd synthesis, the weight of fatty acids is multiply by a factor of 1.04 to convert it to the weight of triglyceride oil (Eqn. 1.3).

$$Oil\ length = \frac{Weight\ of\ "oil"}{Weight\ of\ all\ ingredients - water\ evolved} \times 100 \qquad (Eqn\ 1.2)$$

$$Oil\ length = \frac{1.04\ \times Weight\ of\ fatty\ acids}{Weight\ of\ all\ ingredients - water\ evolved} \times 100 \qquad (Eqn.\ 1.3)$$

In this classification, alkyds are divided into three different groups namely

i. Long oil alkyds- oil content higher than 55 %
ii. Medium oil alkyds – oil content between 45 % to 55 %
iii. Short oil alkyds – oil content of less than 45 %

The alkyd classification may vary from formulator to formulator as the dividing lines between these classes may be slightly different, normally by only a few percent. Resin formulated with oil content higher than 75% is no longer considered as an alkyd resin but modified oil instead.

Oil length also influences the alkyd properties and their end users applications. Long oil alkyds are soluble in aliphatic solvents and have lower surface tension hence better wetting properties. Moreover, they are capable of air-dry in 5 to 8 hours and easily applied by brush which makes them suitable to be used as binder in building interiors and Do-It-Yourself paints. On the other hand, short oil alkyds are compatible with aromatic solvents and exhibit higher viscosity and hardness compared to alkyds with longer oil length. Their applications are restricted to industrial coatings such as stoving enamels, car refinishes, anticorrosive primers and road paints. Figure 1.5 illustrates the general properties related to the oil length of alkyd resins.

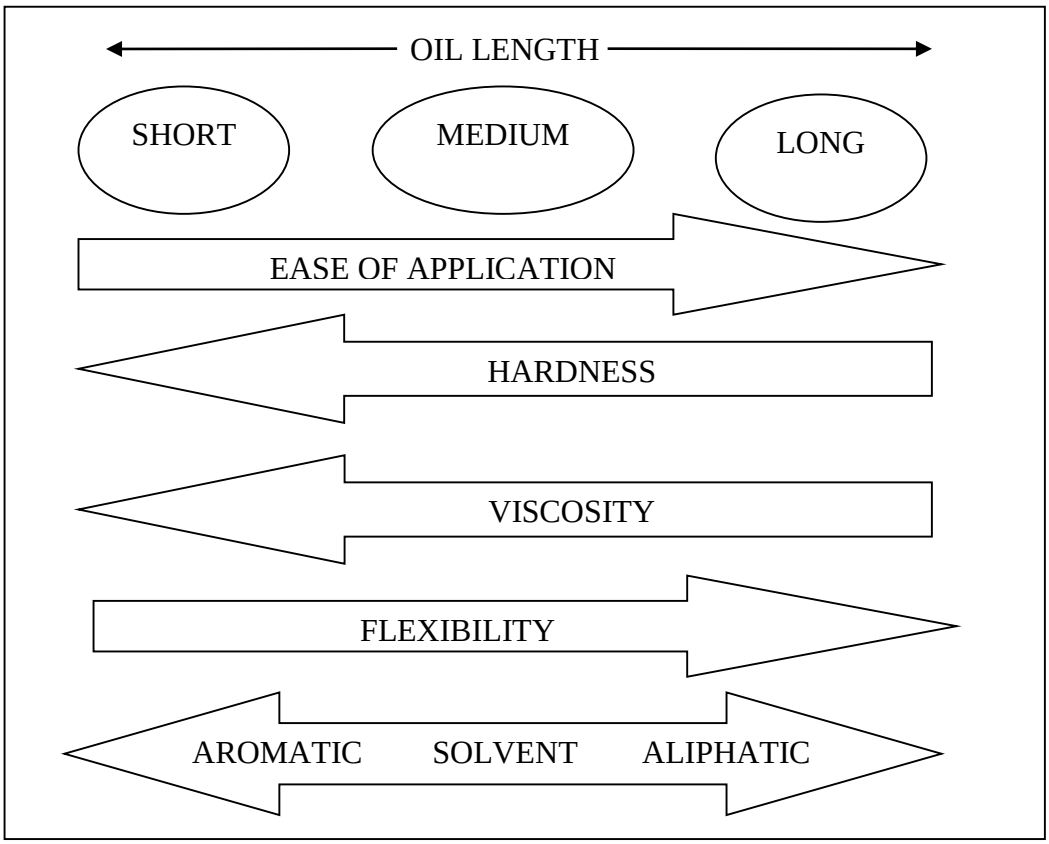


Figure 1.5: Relationship of oil length with the general properties of alkyd resins

1.3.6 Modification of alkyds

Alkyds are modified with the purpose of improving the performance and specific properties of the resin such as drying, application, exterior resistance or corrosion resistance. Modification may be done either by direct mixing with other polymers, or by chemical modification which focused on the reactive double bond in the pendant fatty acid moieties or functional groups that present along the alkyd chains such as the free hydroxyl and carboxyl groups (Stoye, 1996).

(a) Modification by reaction of double bonds of alkyd

The unsaturated sites in the fatty acid chains of alkyds can undergo copolymerisation with vinyl compounds, such as styrene, vinyl toluene, or (meth)acrylic acid derivatives. This process is carried out at controlled temperature of 130 to 160 °C where relevant vinyl monomers are added into the alkyd resins together with peroxide initiator or any other radical polymerisation initiators. A solvent is normally added to the alkyd prior to monomer addition, in order to have better control of the reaction. The modified alkyds are not only better in terms of their drying ability but also have improved resistance towards water and alkali and less prone to yellowing. However, they have low compatibility with aliphatic solvents and are scratch-sensitive (Deligny & Tuck, 2000).

(b) Modification by reaction of functional groups of alkyd

Alkyd contains hydroxyl and carboxyl groups which permits chemical modifications in order to improve their specific properties such as drying, gloss finishing or chemical resistance. While the hydroxyl groups react with mono- or diisocyanate to form urethane alkyds, the carboxyl groups may form thixotropic resins through high temperature reaction with polyamides, or else may react with epoxy resins in order to improve paint adhesion to metal substrate (Stoye,1996).