EFFECT OF POLYETHYLENE GLYCOL AND SILICA-BASED FLAME RETARDANT MATERIALS ON PROPERTIES OF ULTRAVIOLET CURABLE PALM OIL RESIN

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LIST OF SYMBOLS

atm	Atmospheric pressure
AELO	Acrylated epoxide linseed oil
ASTM	American society for testing material
Br	Bromine
cm^3	Cubic centimeter
C=C	Carbon-carbon double bond
$CHCl_3$	Chloroform
Cl	Chlorine
CO	Carbon monoxide
CO_2	Carbon dioxide
DAEMPS	Di(acryloyloxyethyloxy) methyl phenyl silane
DMPS	Dimethoxy diphenyl silane
EMO	Epoxy methyl oleate
EPO	Epoxide palm oil
EPOP	Epoxidized palm oil product
EPOLA	Epoxidized palm oil acrylate
ESO	Epoxidized soybean oil
F	Fluorine
FTIR	Fourier transform infrared spectroscopy
g	Gram
GMA	Glycidyl methacrylate
GPC	Gel permeation chromatography

HEA	2-hydroxyethyl acrylate
HDPE	Hot pressed polyethylene film
HNMR	Hydrogen nuclear magnetic resonance
H·	Radicals of hydrogen
I	Iodine
KBr	Potassium bromide
KI	Potassium iodide
KOH	Potassium hydroxide
L	Liter
LOI	Limited oxygen index
mg	Milligram
min	Minute
mL	Milliliter
mm	Millimeter
mol	Molar
MA	Maleic anhydride
MEK	Methyl ethyl ketone
MG	Monoglyceride
MMA	Methyl methacrylate
MPa	Megapascal
M_w	Molecular weight
nm	Nanometer
N	Normality
N_2	Nitrogen
NaOH	Sodium hydroxide

$Na_2S_2O_3$	Sodium thiosulphate
O_2	Oxygen
OH	Hydroxyl group
OH·	Radicals of hydroxyl
pph	Part per hundred
PA	Phthalic anhydride
PEG	Polyethylene glycol
PEPA	Caged bicyclic phosphate containing epoxy resins
PDI	Polydispersity index
PI	Photoinitiator
Pi·	Excited photoinitiator
PiR·, PiR’·	Radical fragments of the photoinitiator
PF	Phenol formaldehyde
POC	Phosphor organic compounds
POR	Palm oil based resin
PVC	Polyvinyl chloride
R, R’, RH	Hydrogen donor
R^-	Polymer alkyl radicals
RO^-, ROO^-	Oxidative radicals
ROOH	Carboxylic acid
s	seconds
Si-POR	Resin with silane (Si-POR)
SO	Soybean oil
SOPE	Soybean oil phosphate ester
SVOCs	Semi-volatile organic compounds

TAEPS	Tri(acryloyloxyethyloxy) phenyl silane
TEA	Triethylamine
THF	Tetrahydrofuran
TGA	Thermogravimetric analysis
T_b	Boiling point
T_f	Flash point
T_g	Glass transition temperature
T_m	Melting point
TMOS	Tetramethyl orthosilicate
TMOS-POR	Resin with TMOS
TMPS	Trimethoxy phenylsilane
TMPS-POR	Resin with TMPS
UF	Urea formaldehyde
UPR	Unsaturated polyester resin
UV	Ultraviolet
VOCs	Volatile organic compounds
VTMS	Vinyl trimethoxysilane
VTMS-POR	Resin with VTMS
%	Percentage
°	Degree
ºC	Degree Celsius
η	Refractive index
µL	Microliter
>	Greater than
<	Less than

KESAN BAHAN POLIETILENA GLIKOL DAN PERENCAT API BERASASKAN SILIKA DALAM SISTEM TERMATANG SINARAN ULTRA-UNGU YANG BERASASKAN MINYAK KELAPA SAWIT

ABSTRAK

Sistem termatang sinaran ultra-ungu yang berasaskan minyak kelapa sawit (POR) telah dirumuskan malalui pengubahsuaian minyak kelapa sawit dengan gliserol dan glisidil metakrilat (GMA). Polietilena glikol (PEG) dan monomer berasaskan silika (silina) digunakan sebagai agen pelembut dan perencat api. Vinil trimetoksi silina (VTMS), fenil silina trimetoksi (TMPS) dan tetrametoksi silina (TMOS) adalah antara silana yang digunakan dalam kajian ini. Sifat fizikal, mekanik, kestabilan haba dan perencat api telah dikaji. Keputusan menunjukkan kehadiran PEG telah menurunkan berat molekul POR dan mempunyai indeks kepoliserakan (PDI) dalam linkungan 1.69 hingga 2.30. Selain itu, POR mempunyai nombor iodin tinggi daripada 130g I_2/100g minyak dan boleh disifatkan sebagai minyak pengering walaupun nombor iodin mengalami sedikit penurunan selepas penambahan PEG. Setiap filem termatang menunjukkan tahap permatangan yang tinggi dan mempunyai kandungan gel melebihi 95%. Keputusan tersebut juga menunjukkan semua silina diikat secara kimia pada polimer struktur POR. Kesan pelembutan yang dibawa oleh PEG telah meningkatkan kesan penembusan resin, kebolehlenturan filem, kekuatan lekatan, kebolehbasahan dan penyerapan air kayu terlitup. Keupayaan silana untuk berinteraksi dengan kumpulan hidroksil dalam POR dan permukaan kayu telah menurunkan kesan penembusan resin, kebolehbasahan dan penyerapan air kayu terlitup. Dengan itu, kekuatan lekatan kayu telah meningkat dari 2.50MPa ke

3.81MPa selepas penambahan silina. Sampel yang mengandungi TMPS menghasilkan kestabilan haba dan kesan perencat api yang tertinggi di antara semua silina. Suhu degradasi filem telah meningkat ke 390ºC, manakala oksigen indeks terhad (LOI) kayu terlitup telah meningkat dari 22.15% ke 25.35%. Secara keseluruhannya, penambahan silina dalam formulasi telah menghasilkan filem dan kayu terlitup dengan kestabilan haba dan kesan perencat api yang tinggi.

EFFECT OF POLYETHYLENE GLYCOL AND SILICA-BASED FLAME RETARDANT MATERIALS ON PROPERTIES OF ULTRAVIOLET CURABLE PALM OIL RESIN

ABSTRACT

An ultraviolet curable palm oil resin (POR) was formulated by modifying palm oil with glycerol and reacted with glycidyl methacrylate (GMA). Polyethylene glycol (PEG) and silica based monomers (silanes) were employed in the formulation as softening and flame retardant agents. The silanes were vinyl trimethoxysilane (VTMS), trimethoxy phenylsilane (TMPS) and tetramethoxy silane (TMOS). The physical, mechanical, thermal stability and flame retarding properties of Si-POR were studied. The results showed POR with PEG has smaller molecular weight and polydispersity index (PDI) ranged from 1.69 to 2.30. It was noticed that iodine number of POR was greater than 130g I_2/100g oil and can be characterized as drying oil, though the iodine number was declined slightly in the addition of PEG. From gel content analysis, each UV cured films showed a high degree of curing with gel content more than 95%. The results indicated all the silanes were bonded chemically onto the chemical structural of POR polymers. The softening effect brought by PEG has increased the penetration effect of the resin, film flexibility, pull off strength, wettability and water absorbability of the coated wood. The ability of silane to interact with hydroxyl groups of POR and wood surface has lower the penetration effect of the resin, the wettability and water absorbability of the coated wood. Subsequently, the pull-off strength of coated wood was increased from 2.50MPa to 3.81MPa after silane was added. Among the silanes, the sample with TMPS yielding the highest thermal stability and flame retardant properties. The degradation temperature of the film was increased to 390ºC, while the Limited Oxygen Index (LOI) of coated wood was enhanced from 22.15% to 25.35%. In overall, the additional of silane content in the formulation had enhanced thermal stability and flame retarding properties of the films and the coated wood.

CHAPTER 1

INTRODUCTION

1.1 Problem statement

Recently, there are many attempts have been carried out to develop environmentally compatible product due to the awareness of environmental issues and the potential of renewable resources to produce value added product. For instance, Lee & Deng [1] prepared polyurethane from lignin and soybean oil with a higher content of the renewable materials, whereas Dai et al. [2] synthesized bio-based polyester resin for ultraviolet (UV) curable coatings material. Meanwhile, Giuntoli et al. [3] prepared a coatings material from renewable resources for protection of bronzes.

The popularity of renewable resources as a raw material is attributed to their availability, low cost, and non-toxic [4–7]. One of the popular renewable resources that have been used to produce an environmentally compatible product is vegetable oil [8]–[10]. Owing to depletion of petrol based chemical, it is expected that it would be exhausted in the year 2050 [11 & 12]. Therefore, renewable resources like vegetable oil has become more important. Vegetable oil is triglycerols of the fatty acids, which have a glycerol backbone linked to three fatty acids chains [13–17]. Vegetable oil also can be used as one of the materials to replace the traditional used of petrol based chemicals. In general, the advantages of using vegetable oil include its ready availability of starting materials, non-depletable and biodegradable [18–21]. Attractive properties of long chains and specific structural of vegetable oil, make it suitable for producing various industrial products such as plasticizers, lubricants, adhesives, packaging materials, printing ink, paint and coatings [22 & 23].

There are various types of vegetable oil available in the market. For instance, palm oil is extracted from oil palm kernel in its fruit mesocarp, sunflower oil from sunflower seed and others as well. They have high nutrition content, mostly used as food ingredients for texture and flavour purposes, in the food industry as the cooking oil [24 & 25]. Some of them are used in industry products, such as the soap, candles, skin products, shampoo, and perfumes. Other than that, they also have been used as the raw precursors in the production of polymeric materials in chemical industry [26–28]. Normally, utilization of vegetable oils in polymeric materials production is influenced by their production capacity, which leads to more economical price and easily available. In Malaysia, palm oil normally is chosen among the vegetable oils for its high oil production per unit area of plantation [29]. Thus, palm oil is believed suitable to be used as a raw material in various studies to produce resin [30–32].

The UV technology is categorized as a green technology in solving emissions of Volatile Organic Compounds (VOCs) issue since UV curable resin does not involve VOCs in the formulation, while the traditional coating methods are usually high in energy consumption and emit harmful by-products [33–37]. Although some improvement had been made, it still does not meet the zero VOCs requirement. Other than reducing VOCs emissions and environmentally friendly purposes, UV curing technology is popular with high curing rate, room temperature operation, low energy consumption, and high quality end products [38–43]. Combination of renewable resources like vegetable oil in UV curable resin giving a “green + green” solution in overcoming the environmental issues [44–46].

1.2 General background

Pam oil is obtained from the mesocarp of oil palm fruit. Historically, oil palm (Elaeis guineensis) was originated from Africa and introduced to Malaysia since 1875 [47]. The first commercial planting was established in 1917 at Tennamaran Estate in Kuala Selangor [48]. Nowadays, it is a main renewable resource for the world's food, oleo- chemical and biofuel industries [25 & 29]. About 90% of palm oil is used for edible purposes, such as the manufacturing of margarine, deep fat frying, shortening, ice creams, cocoa butter substitutes in chocolate. While the remaining 10% is used for soap and oleochemical manufacturing [49].

Besides, palm oil has been used as a raw material in various studies to produce polymer resin. However, some of the resins show a poor degree of crosslinking due to the low unsaturation in palm oil molecules [50]. According to Edem [25], iodine number of palm oil is in range of 47-55.83 g I_2/ 100g oil and it is classified as a non-drying oil. Thus, chemical modification is necessary to impart higher functionality to palm oil chain. Incorporation of monomer which carries specific function into the final products can be one of the modification methods. However, the monomers should follow a few criteria to enhance the degree of UV curing and avoid chemical migration into the environment. According to Randoux et al.[51], additives consist of multifunctional groups can be attached to palm oil chain through a reactive route. Subsequently, it bonds chemically onto the polymer backbone. For instances, an epoxidized palm oil (EPO) is a suitable precursor for further chemical reaction [31 & 52]. According to Rosli et al.[31], long fatty acid chains of EPO had improved the flexibility of the resin. On the other hand, palm oil is converted to polyol or monoglycerides through alcoholysis with glycerol [26 & 53]. The palm oil based monoglycerides are chemically modified by introducing acrylate monomers which consist of carbon-carbon double bonds onto the hydroxyl groups of the monoglycerides [54]. The chemical modification was done to improve the ultraviolet curability and increase the quality of the final coating. Tanaka et al.[26] had produced polyurethane foams from monoglycerides, polyethylene glycol (PEG) or diethylene glycol and an isocyanate compound, while Rozman et al.[32] had synthesized a UV curable resin based on palm oil. The resin was prepared through etherification of the monoglyceride with glycidyl methacrylate (GMA). The resin can be cured using UV radiation, but it was too brittle. Hence, further investigation is necessary

On the other hand, the flame retardant agent is necessary to be employed in the coatings formulation to enhance its flame retarding properties. The suitable flame retardant agents such as silanes usually consist of multifunctional groups, which allows it to react with other polymeric materials [51]. If follows an additive route, flame retardant needs at least 30% by polymer weight to gain a good performance in flame retarding properties. While through a reactive route, it needs a smaller amount to achieve the same result [51 & 55]. However, the high amount of flame retardant added through the additive route give an adverse effect on the mechanical properties of the polymers. In addition, reactive type flame retardant distribute itself homogenously between the polymeric chains, to interact with the polymer chains and give enhancement to the specific properties of the end product [98]. Therefore, reactive type flame retardant achieves greater interest from researchers.

1.3 Scope of study

From the previous studies [32 & 56], UV curable coating prepared from palm oil and GMA was brittle and highly flammable. Hence, a softening agent- polyethylene glycol (PEG) was employed to enhance the flexibility of the palm oil based resin (POR). While different types of silica-based flame retardant materials were incorporated into the formulation to enhance the flame retarding properties. The silica-based or silane flame retardants were vinyl trimethoxysilane (VTMS), trimethoxy phenylsilane (TMPS) and tetramethoxy silane (TMOS). These silane flame retardant agents are expected to interact with POR polymers at room temperature, in the presence of triethylamine (TEA) as the curing agent. In addition to the purpose of flame retarding enhancement, the silane also is acting as a monomer in the formulation. The UV curability of the resin was determined by the gel content test. The penetration effect of the resin, wettability and water absorbability of the coated wood were studied by contact angle analysis. In addition, the hardness and thermal stability of film, and the pull-off strength of the coated wood will be studied. The flame retarding properties of the coated wood was determined by Limited Oxygen Index (LOI), UL 94 and Methenamine Pill test.

1.4 Objectives

Hence, the objectives of this study were:

a. To prepare the UV curable resin from palm oil (POR);

b. To study the properties of POR with different types of silica-based flame retardant materials;

c. To determine the flame retarding properties of coated wood with flame retardants from the prepared POR;

d. To measure the penetration effect of the resin, wettability and adhesion properties of the coated wood.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

Palm oil is a non-drying oil. The drying properties of palm oil can be changed through the chemical modification with acrylate monomers. According to Rosli et al.[31] and Rozman et al.[32], palm oil can be converted to epoxide or monoglyceride as a raw precursor before further modification with acrylate monomers. Recently, interest has been developed in the modification of renewable polymers with functional monomers to enhance its flame retarding properties [57–59]. Subsequently, the resin prepared can be applied as a layer of coatings on a substrate surface to increase its flame retarding properties. In addition, the flexibility of the coatings is vital to avoid cracking and peeling off during combustion.

2.2 Ultraviolet curing technology

Radiation cure, high solids, and waterborne coatings have attracted high intensities from researchers for the reduction of volatile organic compounds (VOCs) emissions and meet the environment regulation requirement [60–65]. Radiation curing technology is one of the solutions to solve the problems. Historically, it has been introduced since the 1960s [66].

Ultraviolet (UV) curing technology is one of the radiation curing technology. It uses the UV radiation with electromagnetic spectrum 100-400nm to initiate the polymerisation to transform a liquid resin into a solid film (coherent film) [42 & 64]. It can transforms 100% of the reactive components, especially the liquid resin into solid in the presence of UV radiation.

Three major components involved in UV curing technology. i.e. (i) UV source to generate the UV radiation, (ii) resin with the unsaturated group and (iii) photoinitiator. Nowadays, mercury arc lamp retained in quartz tube containing mercury vapour and an inert gas at fixed pressure is utilised as the UV radiation source in UV machine [66]. Photoinitiator is used in small amount in the UV curable system. It absorbs energy from UV radiation and forms an active radical or ions to initiate polymerization. Selection of photoinitiator is done according to the radiation source, film thickness, the pigmentation and types of resin used [60].

Acrylated resin found to be more suitable to undergo UV curing for the reasons of high acrylation content and exhibit high reactivity to react with other unsaturated components to produce a dry and clear film when exposed to UV radiation [61, 67–69]. Example of the acrylated resins or oligomers are epoxy acrylates, polyether acrylate, urethane acrylates, and polyester acrylates [67]. The general types of unsaturation that are suitable to undergo UV curing is shown in Figure 2.1.

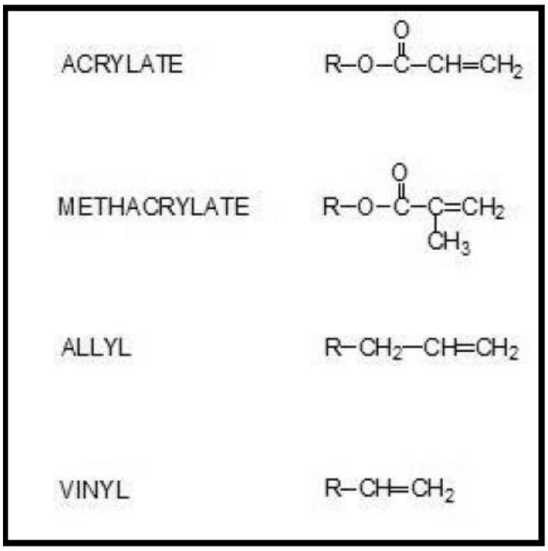

Figure 2.1 Types of unsaturated components suitable for UV curing [67].

A higher degree of acrylation or amount of unsaturation shortens the curing time of the coatings material [32, 70 & 71]. In addition, the performances of the end products can be improved too. Since the increment of unsaturation content increases the crosslink density of coatings, consequently, it improves film hardness, gained excellent adhesion and tensile strength of coatings, exhibits good water resistance, higher thermal stability of the end products [68 & 77]. Different types of acrylate compound produced products with different performance. Generally, epoxy acrylate increases the reactivity of resin, enhances the hardness and chemical resistivity of UV cured film. Urethane acrylate shows greater flexibility, toughness and weathering properties of the products. Moreover, it also reduces the yellowing effect of the coatings. While polyester acrylate enhances the wettability and reduces the viscosity of the resin [42].

In general, there are two types of polymerisation involve in UV curing technology. Free radical polymerisation is the most common. While UV cationic curable system only stands for a small portion of the UV curing markets. In the comparison of the UV free radical polymerisation, UV cationic system is sensitive to humidity and limit by its basic materials. Moreover, it also takes a longer time to cure [42].

Figure 2.2 shows free radical UV polymerisation mechanism. According to the figure, free radical UV polymerisation is a chain growth reaction. It involves of three main steps: initiation, propagation, and termination. Free radical formation is the first part of the initiation, and later addition of free radical to a monomer. It is followed by next step- propagation, which includes the growth of monomer by continuous addition of monomers. Each addition can form a new radical. The propagation is terminated when no more radical is available. After reaching the limit of mobility or viscosity of growing polymer, chain transfer occurs when the polymer extracts a hydrogen atom from a donor molecule. Thus, a new polymer is formed.

Radical Formation	$\mathrm{Pi} \xrightarrow{h_v} \mathrm{Pi}\cdot$
Initiation	$\mathrm{Pi}\cdot + \mathrm{R} \longrightarrow \mathrm{PiR}\cdot$
Propagation	$\mathrm{PiR}\cdot + \mathrm{R'}\cdot \longrightarrow \mathrm{PiRR'}\cdot$
Chain Transfer	$\mathrm{PiRR'}\cdot + \mathrm{R''H} \longrightarrow \mathrm{PiRR'H} + \mathrm{R''}\cdot$
Termination	$\mathrm{PiRR'}\cdot + \mathrm{PiRR'}\cdot \longrightarrow \mathrm{PiRR'R'RPi}$

Whereby;

Pi = Photoinitiator

Pi· = Excited photoinitiator

R, R’ = Hydrogen donor

PiR, PiR’· =Radical fragments of the photoinitiator

Figure 2.2 Free radical UV polymerisation [72].

Advantages of UV curing technology are: (i) room temperature operation and energy saving; (ii) minimal space required; (iii) high curing rate; (iv) resin cure only when to expose to UV radiation; (v) solvent free and inhibit the emission of VOCs; (vi) less waste generated; (vii) environmentally friendly; and (viii) excellent performances of the products [54, 61, 65 & 70]. However, the penetration of UV curing is weak if the thickness of the resin applied on the substrate is too high and opacity for curing is limited [73]. Subsequently, a thinner and transparent resin is suitable to allow penetration of UV curing. In addition, the UV curing equipment investment is relatively large [36]. But the price is reimbursed from the energy saving in the long term application.

UV curing technology has been used for drying printing ink on plywood for building materials [54]. Now, it is widely used in different applications, from the fast drying wood and plastic coatings, automotive applications, graphic arts printing inks, hot melt pressure sensitive adhesive and structural adhesive for bonding glass, ceramics, plastic and metal [61 & 70].

2.3 Renewable resources

Renewable resources, derived from water, carbon, and sunlight through photosynthesis. This material could be a product obtained from individual plants, which then utilized for different human needs such as food, shelter, environmental protection, and others. In general, they are easily available, cheap materials, non-toxic, non-volatile, renewable and biologically degradable [76–80].

Depleting of the petroleum based product has devoted to the demand of renewable resources to produce biodegradable and value added products. Many researches based on the renewable feedstock were done and increased over the past few decades. This is attributed to the limited fossil resources, the increase in oil prices, environmental issues, health hazards, and consumers interests to use eco-friendly products [6, 8 & 62]. Owing to these reasons, coating industry has transformed into a ‘greener’ industry by using bio-derived ingredients and some green technologies to tailor several end use applications [63].

There are some advantages on the usage of these natural-based materials, which include environmental friendly process, low energy consumption, limited waste production, reduction of organic solvents in coatings, less VOC emission and better performance of products comparable to the petrol derived products [4, 8 & 23].

Therefore, the renewable resource has enormous potential, significance, and applications in the industrial world.

2.4 Category of vegetable oils

As mentioned in the previous chapter, vegetable oil is made up of a glycerol backbone linked to three fatty acids chains [15]. Fatty acids stand for 95% of the composition of vegetable oil and their content are distinctive for each vegetable oil [8]. The chemical structure of different fatty acids and their composition are shown in Figure 2.3 [8]. As refered to Figure 2.3, several functional groups are available on the fatty acids chains. They are varied from the hydroxyls, carbon-carbon double bonds, epoxies, esters and others [23]. Hence, they are capable of being used for direct polymerisation or modification of vegetable oil to obtain desire polymer.

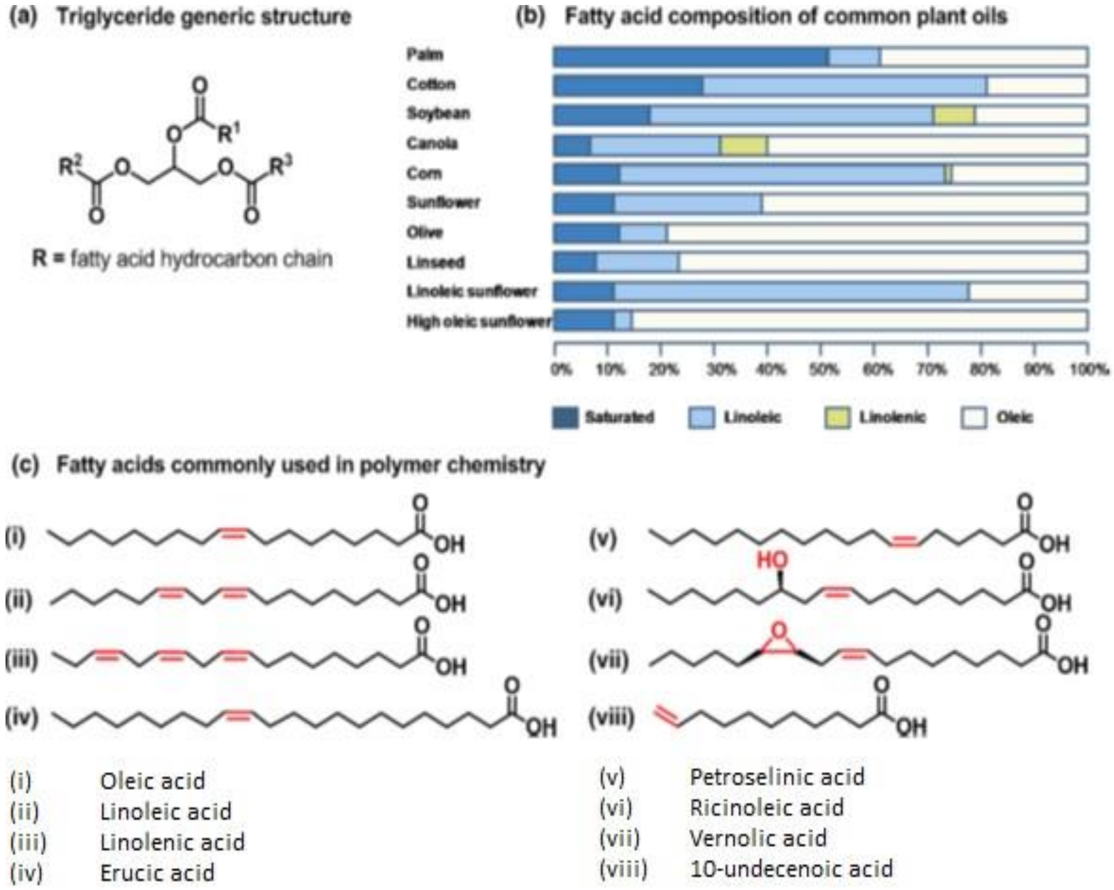

Figure 2.3 The chemical structure for different fatty acids and their composition [8].

Ordinary, vegetable oil is classified into three classes. I.e. (i) Non-drying oil (iodine value less than 115); (ii) semi-drying oil (iodine value between 115 and 130); and (iii) drying oil (iodine value bigger than 130) [8, 9 & 81]. Iodine number is the mass of iodine in g that was consumed by 100g of the chemical substance. It is an analysis method used for the determination of unsaturation in hydrocarbons, such as vegetable oil.

Vegetable oil has a high tendency in producing polymeric materials for binder and coatings [18, 28, 36 & 44]. It has been started to be utilised in coating applications since the 1950s [4]. Vegetable oils, especially drying and semi-drying oils are potential to dry and form coherent films in their original forms, depending on their inherent properties, unsaturation content, conjugation or non-conjugation and the chemical structure [23, 82 & 83]. Drying and semi-drying vegetable oils are able to form polymeric materials with crosslinked structures through the reaction with free radicals presence in the air. The product based on them show higher curing rate, better adhesion, resistance to alkali and acid as compared to non-drying oil [82]. As for non-drying oil, it needs to undergo chemical modification to incorporate suitable and active functional groups like hydroxyls, vinyl or acrylics structures to the oil before forming films [23, 54, 84 & 85].

Besides the natural drying characteristic, vegetable oil also improves the flexibility retention and fluidity characteristic of the coatings [83]. The long fatty acids chain of the vegetable oil enables it to produce free flowing resin without using any solvent. These make them suitable to be used as reactive diluents in solventless coatings [4].

Several resins can be made based on the plant oils, including the polyester, polyurethane, polyamides, vinyl polymers, and epoxy resins [19, 28, 44, 46 & 86]. However, the products manufactured from vegetable oils without additional of other chemicals has low mechanical properties. Through several researches, the modified triglyceride has very well definite linear structures and three-dimensional network. Hence, it is suitable to be used as matrices for bio-composite and hybrid materials. The introduction of others functional groups or modification is vital to improve its characteristics. For example, the incorporation of epoxies to the vegetable oils improves the toughness of the products [23]. The formation of polyester and polyurethane based on the vegetable oils enhance the scratch hardness and impact resistance [16 & 28].

2.4.1 Development of vegetable oil based resins

Vegetable oil based resins can be prepared through two main routes, either directly as a raw material or indirectly as a raw precursor. These two routes are mainly chosen depending on the unsaturation content in the vegetable oil, that is dry and semi-drying oils which are suitable for both as a raw material and precursor, while non-drying oil is applicable only as a raw precursor [54, 82–84 & 87].

Both drying and semi-drying oil have iodine value higher than 130 and 115-130, respectively [8, 9 & 81]. They are dried easily in the atmospheric condition and able to act as a raw material without forming precursor in the preparation of a resin. Alam et al.[23] suggested self-cured vegetable oil coatings prepared with sufficient unsaturation, no matters by the original drying or semi-drying oils, or acrylated non-drying oil, which does not require any solvent and VOCs in the formulation can be avoided [23]. Thus, drying and semi-drying oil are suitable for the making of the dry and hard surface coating [81–83]. Linseed, castor, tung, perilla *(Perillu frutescens)* and oiticica *(Licania riguda)* are examples of the drying oils [15, 82, 88–92]. Linseed oil, obtained through mechanical expelling from the *Linum usitatissimum* (a flax plant), as high α-linolenic acid content give rise to high iodine value at a range of 175-204 [89]. Derksen et al. [4] reported that high unsaturation of linseed oil allows it to undergo autoxidation and forming tough films. They also mentioned that tung oil contains over 70% of eleaostearic acid, which is a fatty acid with three double bonds conjugating rather than methylene interrupted as in linolenic acid. This structure allows it to cure at a higher rate than linseed oil. The coatings based on tung oil were UV sensitive and the films formed were more rigid as compared to linseed oil films [4].

Ge et al.[90] had synthesized an acrylate modified tung oil water insulation varnish from maleic anhydride (MA) and other acrylates. They found that the increment of acrylates constant had improved thermal stability and hardness of the coatings. However, further increase of acrylates content until a certain limit, the flexibility and adhesion start to decrease [90].

Huang et al.[63] had prepared UV curable tung oil based resin with various acrylate compounds, including MA, 2-hydroxyethyl acrylate (HEA) and GMA. According to them, epoxy ring from GMA could react with a carboxyl group and generate a new hydroxyl group, which gained through Hydrogen Nuclear Magnetic Resonance (HNMR) and Fourier Transform Infrared (FTIR) Spectroscopy. The resins produced had a broad molecular weight and polydispersity index (PDI) range from 1.70 to 2.20 due to the complex side reactions. They also found that higher content of MA had produced a resin with narrower molecular distribution and PDI. The higher amount of acrylate compound presence had improved the curing rate, glass transition temperature (T_g) and decomposition temperature. The cured films showed good thermal stability with the decomposition temperature at above 350ºC, which made it suitable to be used as a coatings material for high temperature application [63].

Mahendran et al.[22] had used epoxidized linseed oil to prepare an acrylated epoxidized linseed oil (AELO). The resin was later mixed with three different types of photoinitiators at different concentrations. They concluded that better properties of the AELO based coating were prepared, depending on the suitable photoinitiator, although the increase of the concentration of photoinitiator had reduced the drying time as well [22].

Safflower is another example of drying oil, which has an iodine value range from 136-148. It has non-yellowing properties, which is attributed to the linolenic acids presence in their compositions, as soybean oil does. Therefore, they are suitable to be used to manufacture light coloured coatings. Other than that, safflower oil and soybean oil also are suitable to be used in mixing with tung oil to improve the yellowing properties [4].

Soybean oil is one of the semi-drying oils. It contains slightly high unsaturation (iodine value of 120-136), which make it possible to polymerise into other suitable new biomaterials [79, 80, 93 & 94]. Li et al.[83] studied on the cationic polymerization of different types of soybean oil-based resins. The polymers gave properties varied from the soft rubber to hard thermoset, depending on the chemical structure of monomers substituted with the soybean oil. They also found that the polymers were comparable with the conventional plastic, respected the moduli and thermal stabilities of the soybean oil based polymers [83].

Other than soybean oil, sunflower oil is also a semi-drying oil with iodine number in range of 125-144. It is a derivative of sunflower oil, constituents containing mainly free fatty acids and minor content of glycerides and sterolsa [95 & 96]. Del Rio et al.[97] reported that different types of initiator had produced polymers of different chemical structures. The polymer was prepared using different types of initiators from the coordinative polymerisation of epoxy methyl oleate (EMO), which is a derivative of sunflower oil. They found out that the side reaction occurred during the polymerisation of EMO and formed a polymer with branched structures and ester groups at the main chain, which minimizes the usage of the branched EMO in the preparation of renewable polyether polyols. In order to inhibits this problem, a small amount of tetrahydrofuran (THF) as an inhibitor is needed to copolymerize with EMO [97].

Non-drying oil, for example, coconut, almond, olive, peanut and palm oils have a low iodine value. The iodine number is less than 115 [25, 50, 98 & 99]. Hence, modification of non-drying oil is needed to increase the unsaturated content before it can be used as a reactive monomer of resin [76].

According to Islam et al.[84] and Ataei et al.[85], the limitation of carbon-carbon double (C=C) bonds in palm oil (iodine value of 46.33) leads to the poor drying properties of the alkyd resin based on palm oil. This suggested the needs of curing agent and dryer to cure the resin. Different alkyd resins were prepared based on the different composition of acrylates like MA or methyl methacrylate (MMA), to react with the palm oil for improving the hardness and unsaturation, and thus, decrease the drying time [84 & 85]. Ataei et al.[85] found that the increasing number in MMA content had improved the hydrophobicity and provided good adhesion on the steel panel, consequently showed higher resistance to water and salt.

Ang et al. [54] attempted on converting the non-self-drying palm stearin alkyd into environmental friendly UV curable resin through the incorporation of MA and MMA as reactive diluents. They found that the products showed better films properties, shorter curing time, no VOCs emission and better the economy value for the resins [54].

Epoxidized vegetable oil was found as the most popular modification of vegetable oil [36, 41, 76 & 80]. It involves polymerisation of forming new epoxide group through the reaction between alkene and peracid. It is useable for the cationic curable coatings. Besides that, new epoxide group can be incorporated through another route, which is the substitution of an epoxy ring-containing molecule into the oil. For example, glycidyl methacrylate (GMA), allyl glycidyl methacrylate and diglycidyl ether bisphenol A are the suitable monomer incorporated into the vegetable oil [63 & 80].

Rosli et al.[31] had synthesized UV curable epoxidized palm oil (EPO). They found that EPO replaced partially petroleum derived EPO, produced films with good strength and hardness properties, and no post cure of the film is needed [31].

Vegetable oil can be modified by incorporating monomers containing special functions into the final product [99–102]. Before the monomer renders the nature of the products, it is compatible with the polymer structural. Those monomers reduce the modulus and tensile strength, increase flexibility, elongation, impact strength, and tear strength of the resin and even modify the rheological properties of the polymer [99 & 102]. Besides, the flame retardation of polymers is similarly enhanced. For example, phthalic acid esters and phosphororganic compounds (POC) are additives employed due to the ability of both in rendering softening effects as well as in imparting flame retarding properties in several commercial products. These additives have extended properties and types of applications with respect to the polymer resins over a wide range [100].

Jia et al. [92] also proposed the soybean oil-based softener containing flame retardant groups (SOPE) prepared from epoxidized soybean oil (ESO) and diethyl phosphate. Figure 2.4 shows the synthetic route and the chemical structure of epoxidized soybean oil (SOPE). The figure shows that SOPE was made up of main triglyceride backbone connected to several diethyl phosphates, while the diethyl phosphate has two branches also connected to more triglyceride backbone. Later, ESO was used to soften polyvinyl chloride (PVC). The results indicated that the modified PVC has better compatibility, improving mechanical and thermal properties. The decomposition temperature of PVC had improved from 249.4 ºC and reached 275.5 ºC after blended with SOPE. Its Limited Oxygen Index (LOI) value also increased from 24.2% to 33.6%. The melt viscosity and compatibility among the blended PVC have resulted in good adhesion and softening effects [92].

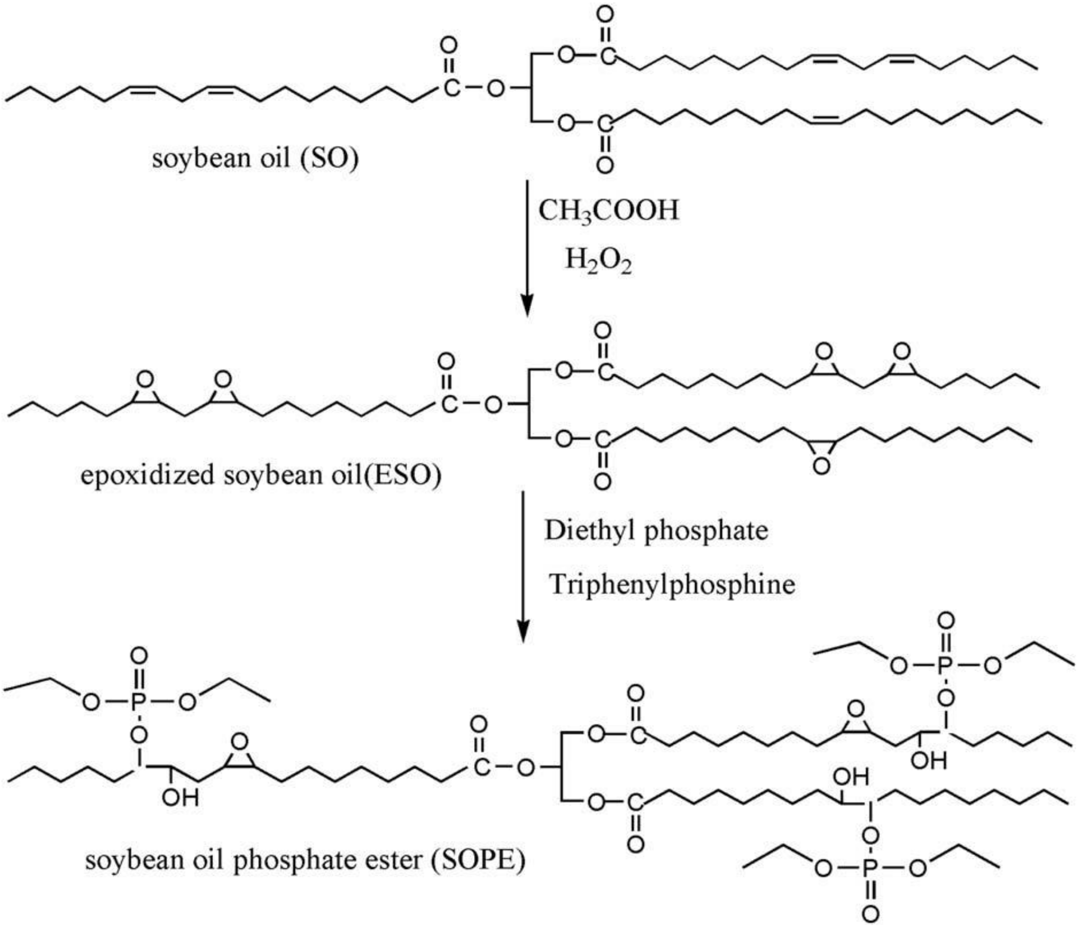

Figure 2.4 The reaction route for the synthesis of ESO and SOPE [92].

2.5 Palm oil based resin

Palm oil is an edible vegetable oil extracted from the mesocarp of the oil palm fruits. The biggest interest in using palm oil as a raw precursor is because of its high production yield and cheaper price than other vegetable oils [29 & 74]. The physiochemical of palm oil is shown in Table 2.1.

Table 2.1 Physicochemical properties of palm oil [25].

	Palm oil
Melting point (◦C)	**34.2**
Relative density (50 ◦C/water at 25◦C)	**0.89–0.92**
Refractive index (*η*)	**1.46**
Moisture and impurities (%)	**0.1**
Iodine value	**47–55.83**
Saponification value (mg KOH/g)	**196–208.2**
Unsaponifiable matter (%)	**0.01–0.5**

The production of vegetable oil based resin usually started from the modification of palm oil. Monoglyceride (MG), the intermediate chemical was prepared through transesterification of vegetable oil. The MG can be prepared by two types of processes; (i) fatty acid process and (ii) alcoholysis process. Alcoholysis or monoglyceride process involve two stages in the alkyd resin preparation. Free hydroxyl groups are produced by the conversion of palm oil by the polyhydric alcohol in the first stage. In the second stage, it is esterified by a polyacid [93]. Meanwhile, a mixture of polyacid, polyalcohol and fatty acids are mixed and heated in only one stage to obtain the alkyd resin in the fatty acid process [32]. Higher quality and better performances of alkyd resin are prepared from the fatty acid process. However, premature polymerisation of the resin prepared from alcoholysis process is prevented easily as compared to the resin prepared from the fatty acid process, due to the easiness of temperature control in alcoholysis process [26]. In addition, alcoholysis process also showed more advantages such as the economical, easy and high processing rate as compared to fatty acids process [104]. Hence, alcoholysis process is popular. Alcoholysis process between vegetable oil and glycerol to prepare MG is shown in Figure 2.5 [32].

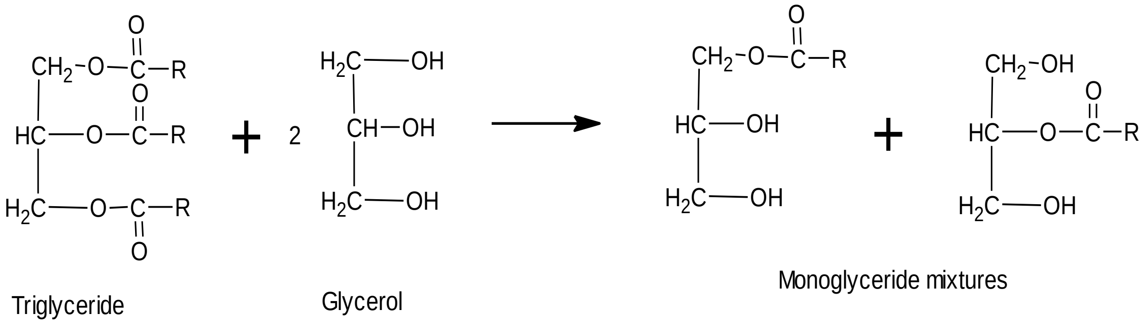

Figure 2.5 Alcoholysis process of triglyceride and glycerol to prepare MG [32].

The MG is later chemically modified to prepare a product with desired properties. For example, the modification of MG with aromatic polymers and polyether improves the thermal stability of the MG while modification with halogenated monomers contributes to the reduction in the flammability of the sample [86]. Chemical modification of the polymer through the incorporation of aromatic flame retardant agent to delay ignition and to reduce the flame spreading rate [51, 69, 101, 105 & 106]. The flame retardant resin can be applied as a layer of coatings on a flammable material, and acted as a protective barrier between the flame and the embedded material in an event of fire. In the flame retardation mechanism, it works efficiently in reducing the heat release rate and mass loss through delaying the propagation of flame [55].

According to Rosli et al.[54], long fatty acid chains of palm oil is able to improve the flexibility and toughness of the resin. They reported that the development of palm oil derivatives such as EPO as a precursor for further chemical reaction with vinyl ether monomers. This is attributed to the poor crosslinking degree due to low unsaturation in the palm oil molecules [31]. Besides, non-drying palm stearin alkyds are used in the production of UV curable resins via fumarization and maleinization. This chemical modification is done by attaching the C=C groups onto the main chain of the polymer to improve UV curability and thus a higher quality of final coating is made [54].

2.6 Flame retardants

Generally, fire occurs from a glowing on the surface of a combustible material with increasing temperature, to create a spark of flame and gradually spread to the whole surface and even the inner content. The process is defined chemically as combustion. In a scientific way, fire occurs in the presence of oxygen and fuel substrate with releasing of heat into the environment. Misuse of fire could destroy our property and lead to death. Protection and prevention are the main ideas of those measurements in reducing fire cases [55 & 107]. The measurements related to fire safety are implemented for product manufacturing, and modify the flame retardancy of the materials for building construction, electrical application, military purposes and others [55 & 108]. Material with flame retardation property is able to retard the growth and propagation of flame, and provide protection from the flame. Sometimes, flame-retarded material is able to self-extinguish as well as slow down the spreading rate of the flame [107].

Flame retardant is a chemical incorporated into a combustible material to retard a flame and reduce the ease of ignition [109], especially for minimizing the hazard of ignition due to the contact with a small fire source such as cigarette and candle [102]. It could be added as an additive or reactive compound through chemical blending or chemically bound to the chemical structure of polymer respectively.

Recently, the development of flame retardant was done based on the multi and reactive functional groups containing a flame retardant. Thus, it is bonded chemically to the polymer backbone and minimize the migration of additive into the environment [97]. Besides, surface modification is another route for the incorporation of flame retardant. This method is widely used in the commercial fireproof coatings, as it is s promising to the combination of flame retarding properties and aesthetic effects on the surface of material along with the preserving mechanical properties of the material. Flame retardant based coatings usually is able to act as a barrier between the fuel and the fire source, having ability to retard the flame, work efficiently in the heat release rate and mass loss properties though delaying the propagation of the flame [98].

Thermal degradation of the polymers started from the decomposition of component parts upon exposure to heat, or bonds broken in the polymer, causing it to depolymerise and break up to potential fuel materials through the free radical process under fire conditions [104]. Chemically said, thermal degradation of a polymer involves: (i) bond cleavage of the weakest bond; (ii) subsequent pyrolysis of smaller molecules; and (iii) reduction of the complexity of the polymer. The volatile and combustible pyrolysis products would be changed into gas phase to fuel the combustion. Besides, smoke is formed when small solid particles and gaseous escaped