ENVIRONMENTALLY FRIENDLY EPOXY AND ALKYD COATINGS DERIVED FROM NATURAL RUBBER

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FACULTY OF SCIENCE
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ENVIRONMENTALLY FRIENDLY EPOXY AND ALKYD COATINGS DERIVED FROM NATURAL RUBBER

ABSTRACT

Environmentally friendly coatings are gaining more attention following the growing concern on the threat of environmental pollutions, as well as the depleting fossil resources that have been exploited to produce surface coating resins and additives for the coating industry. One of the approaches to produce environmentally friendly products is to reduce the dependency on petroleum-derived resources in the coating production. In this work, epoxidized natural rubber was utilised to produce epoxy coatings and alkyd coatings. The epoxidized natural rubber was subjected to UV treatment to reduce molecular weight and subsequently improve its solubility in a wide range of solvents. UV-degraded epoxidized natural rubber (UV-ENR25) was characterized with spectroscopies (FTIR and NMR) and gel permeation chromatography, GPC to confirm the reduction in molecular weight, while retaining its epoxide content. Rubber-based epoxy coatings were produced using two different types of hardeners. The first hardener was pentaerythritol tetra (3-mercaptopropionate) which is a common crosslinking agent used in epoxy coating. The second hardener utilised was naturally-sourced tannic acid. The film properties and thermal stability of both epoxy coatings were investigated using series of test methods comprising of physical, chemical, and thermal analyses. Both coatings, UV-ENR25/PETMP and UV-ENR25/tannic acid showed satisfactory coating properties, comparable to some of the reported petroleum derived epoxy coatings. One of the highlights is the focus on the biodegradability of UV-ENR25/tannic acid coating. Owing to the high natural content in UV-ENR25/tannic acid coatings, the coatings exhibited improved extent of biodegradation compared to the commercially available petroleum-derived epoxy coatings. Liquid epoxidized natural rubber was also utilized in alkyd resin synthesis. It served as a polyol in the synthesis and the effect of incorporating the rubber in alkyd synthesis was thoroughly evaluated. The liquid epoxidized rubber was introduced into the alkyd cook during the polyesterification step, for it to serve as polyol and react with polycarboxylic acid. The film properties and thermal stability of the resultant alkyd coatings were investigated using series of standard test methods, as well as chemical and thermal analyses. The results obtained suggest that the properties of alkyd coatings derived using rubber in the formulation was comparable to the control alkyd which was produced purely from the conventional polyol such as glycerol. The integration of rubber into the synthesis offered equivalent in majority and even improvement in some of the coating properties such as film hardness and film adhesion. In summary, natural rubber derivatives could be used as a sustainable raw material in the synthesis of surface coating resin, and the properties of the coatings could match those produced from petrochemical derivatives.

Keywords: Environmentally friendly coating, epoxy, alkyd, rubber

SALUTAN EPOKSI DAN ALKID YANG MESRA ALAM DIHASIL DARIPADA GETAH ASLI

ABSTRAK

Salutan mesra alam mendapat perhatian yang semakin banyak berikutan peningkatan kesedaran terhadap ancaman pencemaran alam sekitar, serta sumber fosil yang semakin berkurangan disebabkan eksploitasi untuk menghasilkan resin bahan tambahan untuk industri salutan. Salah satu pendekatan untuk menghasilkan produk mesra alam ialah mengurangkan pergantungan kepada sumber yang diperolehi daripada petroleum dalam penghasilan salutan. Dalam kerja penyelidikan ini, getah asli terepoksida telah digunakan untuk menghasilkan salutan epoksi dan salutan alkid. Getah asli terepoksida disinari oleh sinaran ultraungu (UV) untuk mengurangkan berat molekul dan seterusnya meningkatkan keterlarutannya dalam pelbagai pelarut. Getah asli terepoksida yang terdegradasi dengan sinaran UV (UV-ENR25) dicirikan dengan menggunakan spektroskopi (FTIR dan NMR) serta kromatografi resapan gel, GPC untuk mengesahkan pengurangan berat molekul, sementaranya mengekalkan kandungan epoksida. Salutan epoksi berasas daripada getah dihasil daripada dua jenis pengeras yang berbeza. Pengeras pertama yang digguna ialah pentaerythritol tetra (3-mercaptopropionate), PETMP yang merupakan agen penghubung silang yang biasa digunakan dalam salutan epoksi. Pengeras kedua yang digguna ialah asid tannik yang bersumberkan semula jadi. Ciri-ciri filem dan kestabilan haba kedua-dua salutan epoksi dinilai dengan menggunakan pelbagai kaedah ujian yang terdiri daripada analisis fizikal, kimia dan haba. Kedua-dua salutan, UV-ENR25/PETMP and UV-ENR25/asik tannik menunjukkan ciri-ciri salutan yang memuaskan, setanding dengan sesetengah salutan epoksi yang dihasilkan daripada petroleum. Kemampuan salutan UV-ENR25/asik tannik untuk mengalami biodegradasi turut dianalisis. Disebabkan kandungan semula jadi yang tinggi dalam salutan UV-ENR25/asik tannik, salutan tersebut menunjukkan tahap biodegradasi yang lebih baik berbanding dengan salutan epoksi komersial yang dihasilkan daripada petroleum. Getah asli terepoksida cecair juga digunakan dalam sintesis resin alkid. Ia berfungsi sebagai poliol dalam sintesis dan kesan penggunaan getah dalam sintesis alkid telah dinilai dengan teliti. Getah terepoksida cecair ditambahkan ke dalam sintesis alkid semasa langkah poliesterifikasi, untuk ia berfungsi sebagai poliol dan bertindak balas dengan asid polikarboksilik. Ciri-ciri filem dan kestabilan haba yang dimiliki oleh salutan alkid yang terhasil disiasat dengan pelbagai kaedah ujian standard, serta analisis kimia dan analisis haba. Keputusan yang terdapat menunjukkan bahawa ciri-ciri salutan alkid yang dihasilkan dengan menggunakan getah dalam formulasi adalah setanding dengan alkid kawalan yang dihasilkan semata-mata daripada poliol konvensional seperti gliserol. Persepaduan getah ke dalam sintesis menawarkan sifat salutan yang setara dengan alkid yang dihasilkan tanpa getah secara keseluruhan, malah terdapat juga penambahbaikan dalam beberapa ciri-ciri salutan seperti kekerasan filem dan lekatan filem. Secara ringkasnya, derivatif getah asli boleh digunakan sebagai bahan mentah yang mampan dalam sintesis resin salutan permukaan, dan ciri-ciri salutan boleh sepadan dengan yang dihasilkan daripada derivatif petrokimia.

Kata kunci: salutan mesra alam, epoksi, alkid, getah

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LIST OF ABBREVIATIONS

^{1}H-NMR : Proton nuclear magnetic resonance

AOCS : American Oil Chemists' Society

ASTM : American Society for Testing and Materials

DGEBA : Bisphenol A diglycidyl ether

DMBA : N,N-Dimethylbenzylamine

DSC : Differential scanning calorimetry

ENR25 : Epoxidised natural rubber with 25% mol of epoxidation

ENR50 : Epoxidised natural rubber with 50% mol of epoxidation

FTIR : Fourier transform infrared

GPC : Gel permeation chromatography

HAP : Hazardous air pollutant

KLK : Kuala Lumpur Kepong Berhad

LENR50 : Liquid epoxidized natural rubber with 50% mol of epoxidation

LGM : Malaysian Rubber Board

MA : Maleic acid

MEK : Methyl ethyl ketone

PA : Phthalic anhydride

PETMP : Pentaerythritol tetrakis(3-mercaptopropionate)

PHT : Pencil hardness test

SMR : Standard Malaysian Rubber

TGA : Thermal gravimetric analyser

THF : Tetrahydrofuran

TMPTA : Trimethylolpropane triacrylate

UV-ENR25	:	UV-degraded epoxidized natural rubber with 25% mol of epoxidation
VOC	:	Volatile organic compound

CHAPTER 1: INTRODUCTION

1.1 Research background

Green chemistry has stormed to the forefront in recent years due to the worsening environmental pollution around the globe. Other than global warming, the depleting of fossil resources is another reason why environmentally friendly products has been gaining interest from various industries, including the surface coating industry. To manufacture green products, there are two main aspects to emphasise on, which are (i) utilisation of technologies that minimises the release of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) during synthesis or preparation, and (ii) utilisation of raw materials which are derived from natural renewable resources in the production lines.

In coating industry, the green technologies involved minimising emission of VOCs and HAPs in the formulation and/or curing system, and examples include powder coatings, waterborne coatings, and radiation curable coatings. Another approach to produce environmentally friendly products is to reduce the dependency on petroleum-derived resources in the coating production. Raw materials involved in the synthesis of coatings are largely derived from petroleum. For instance, bisphenol A, bisphenol F and novolac are common epoxy resins used in coatings formulation and they are petroleum derivatives. Over-exploitation of fossil fuel will eventually lead to exhaustion of this resource since it is a non-renewable resource. Its restoring rate is much lower than the depleting rate. For sustainable innovation and development, it is therefore important to reduce dependency on fossil fuel resources.

There are efforts to implement natural renewable resources to replace petroleum derivatives such as the use of plant oil to serve as raw materials in the production of coating binders. Some of the notable examples of bio-based polymers produced from renewable resources include chlorinated alkyd resins derived from rubber seed oils (Rau et al., 2012), antimicrobial polyesteramide resins derived from linseed oil (Abd El-Wahab & Alian, 2015), intumescent epoxy resin coatings produced with vegetable compounds, using ginger powder and coffee husk to act as carbon sources (de Sa et al., 2017), as well as bio-based coating material produced from modified acetoacetylated castor oil (Zhu et al., 2020). Plant oil is one of the resources which is widely exploited because it is renewable, non-toxic, domestically abundant, and non-volatile. Most of the innovations involve the use of plant oil as raw materials in producing green coatings, and there are significantly lesser studies on other forms of renewable resources exploited for surface coating production.

In this research, natural rubber was used as renewable raw material in the preparation of coating resins. Natural rubber is one of the abundant natural resources that is under-utilised in coating industry. According to the estimation of international rubber research group on the distribution of the world natural rubber applications (shown in Figure 1.1), majority of rubber is used to produce tyres, which is about 65%. Other sectors include hoses and belts 8%, automotive 7%, medical gloves 6%, footwear 5%, threads 1%, foam 1% and adhesives 1% (Blengini et al., 2017). Introducing natural rubber in coating production lines will further diverse its application. The rubber used in this project was epoxidized natural rubber where some of the unsaturation, C=C in the natural rubber has been converted to epoxide groups. The epoxidized natural rubber were broken down into smaller molecular weight fractions via photo oxidative degradation by mean of UV irradiation or chemical oxidative degradation to improve its compatibility with wider range of chemicals, and to serve as resins for surface coating applications.

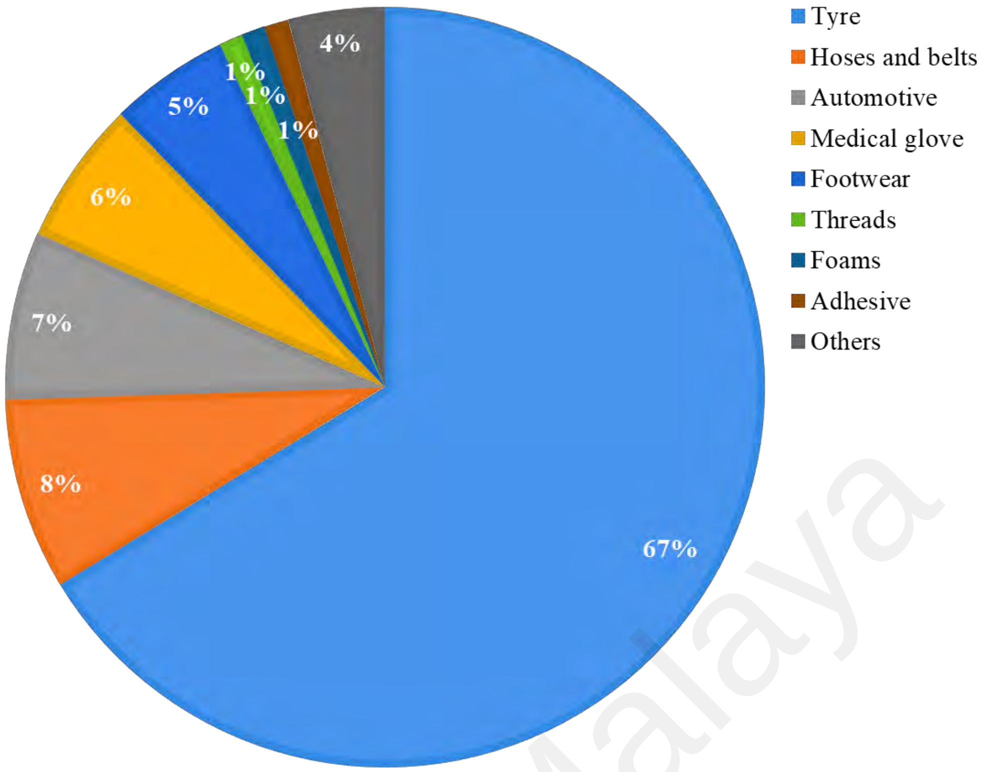


Figure 1.1: Distribution of the world natural rubber applications

The first part of this work focused on the use of the ultraviolet (UV) degraded epoxidized natural rubber to produce epoxy coating. Two separate hardeners were used in this project to produce natural rubber-based epoxy coating, namely pentaerythritol tetrakis(3-mercaptopropionate), PETMP and tannic acid. The former is a typical hardener used in numerous epoxy coating formulations, while the tannic acid which is resourced naturally was chosen as a novel hardener to augment the green nature of the coating. Tannic acid is polyphenol extracted from plants and it is easily available because its production does not depend on climatic conditions and is available in all seasons as it can be obtained from barks, roots, stems and leaves of plants (Boro & Karak, 2017). Epoxy coating produced from the reaction between rubber and tannic acid comprised of high percentage of renewable materials, with both main components in the coating, epoxy resins and hardeners, are derived from natural resources.

To further diverse the application of natural rubber in coating industry, the degraded epoxidized natural rubber was also used as raw material in the synthesis of alkyd resin. The rubber was integrated as part of alkyd by having it to serve as alternative polyol to react with diacids. The epoxide group in the rubber can reacts with the acids via ring opening reaction, and some of the -OH group from the rubber can also form ester linkages with the diacids. This approach of introducing rubber in the alkyd synthesis increases the percentage of renewable resources in the alkyd formulation. Figure 1.2 shows the simplified outline on the focus of this work.

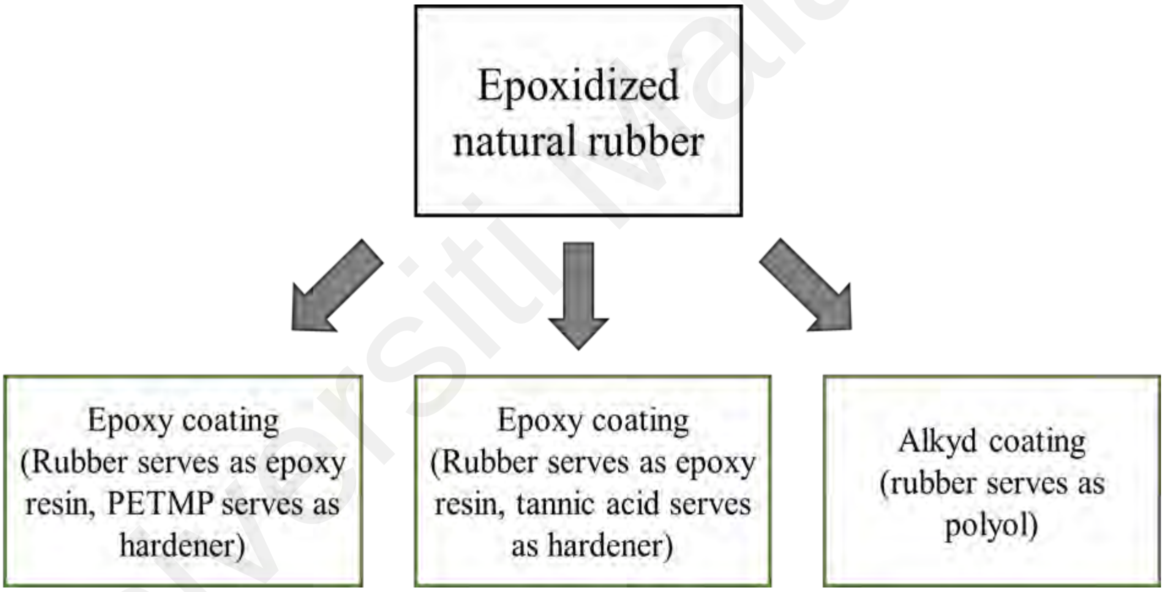


Figure 1.2: Simplified outline on the focus of this work

In summary, this research focused on producing surface coating resins derived from natural resources, specifically natural rubber. Extensive literature review related to the subject matter is given in Chapter 2, while Chapters 3.1 mentions the materials used, Chapter 3.2 to 3.9 details the methodology involved in the preparation of epoxy coating, and Chapter 3.10 until 3.15 are on the preparation of alkyd coating. In the following

Chapter 4.1 expounds about the epoxidized natural rubber, Chapters 4.2 and 4.3, results pertaining to epoxy coatings were discussed, followed by alkyd coating in Chapter 4.4. Conclusion and recommendations made up the final chapter, Chapter 5 of this dissertation.

1.2 Problem statement

Environmental problem and global warming are becoming more severe over the last few decades. Fossil resources are depleting faster than restoring them as non-renewable resource have insufficient rates of renewing ability. It is therefore vital to reduce the dependency on fossil resource. Considering the scarcity of fossil resources and threat from global warming, the use of renewable resources in development of polymeric products becomes highly relevant nowadays. Such trend is observed in various industry, including the surface coatings industries. Unfortunately, the most widely exploited natural resources in development of surface coating resin has mostly been vegetable oils such as soybean oil, canola oil, sunflower oil, and other unsaturated oils only. Other forms of natural resources are often neglected and not thoroughly exploited. One example is natural rubber, a readily available resources but is not commonly exploited in the coating industry. To diversify its application as well as diversify the choice of renewable raw materials in coating sector, natural rubber was used to produce coating resins in this study. This project proposed the use of renewable resources, especially natural rubber in development of novel surface coating resins.

1.3 Research objectives

In trend nowadays, majority industries are transforming their production lines into making more environmentally friendly products in view of the rising threat of global warming and scarcity in fossil resources. This research project took those concern into consideration and aims to utilize more renewable resources in producing added value polymeric product, specifically surface coating resins. To achieve this, following objectives in the project are drawn out:

i. To produce low molecular weight epoxidized natural rubber by means of ultraviolet (UV) degradation.
ii. To utilize the low molecular weight rubber in production of environmentally friendly epoxy coatings.
iii. To incorporate the low molecular weight rubber as the raw materials in alkyd synthesis.
iv. To evaluate the effect of incorporating natural rubber into epoxy and palm oil-based alkyd resin on the film properties of the cured coatings.

1.4 Research significance

Development of environmentally friendly alkyd and epoxy coatings derived from natural rubber is in conformity with the global call to reduce the dependency on fossil resources and at the same time, putting less stress on the environment. Utilising natural rubber as an alternative resource not only diverse the application of natural rubber, but also increases the options of bio-based binders for surface coating formulation. Natural rubber can be a better choice of raw material as it is a form of renewable resource. Performance wise, some improvements are observed in some of the film properties of the coating upon incorporation of rubber into the films. Biodegradability in some of the coating films has improved due to the high content of biodegradable component, natural rubber in the coating systems. Some of the coatings have also demonstrated improved thermal stability and hardness, partly due to the polyfunctionality of epoxidized natural rubber that allows it to provide crosslinking effect in the films.

CHAPTER 2: LITERATURE REVIEWS

2.1 Coatings

2.1.1 Definition and historical development of coatings

Coatings are liquid, paste, or powder which are applied on surfaces by various methods and equipment in layers of given thickness to form adherent films on substrates (Stoye & Freitag, 2008). The purpose of applying coatings includes for decoration, protection, or for special technical properties (Goldschmidt & Streitberger, 2017). For instance, edible coatings are applied onto surface of tablets to preserve and protect their contents and structure as well as modify the release pattern of drug in the tablets (Kurakula et al., 2020). Coatings are applied at the bottom surfaces of deep-sea ships and offshore platforms to protect underwater surfaces from growth of marine fouling organism (Tracton, 2005). Some coatings serve dual function, such as those applied on apparel fabrics are not only for aesthetic purpose, but also to provide permeability from water. Coatings exist for various purposes in every corner of our daily life such as automotive, food and beverages packing, architectural building, electrical items as well as surgery equipment.

Terms “coating” and “paint” are usually confused and used synonymously. “Coating” generally refers a material that is applied to a surface, while ‘paint” is a pigmented material. In other words, paint can be viewed as a specific type of coating material with specific property. Another variation of coatings is lacquer, which recipe was first created around the end of 1st millennium by the monk Rodgerus of Helmarshausen. He reported the detail of its composition and manufacture method in his book, Schedula Diversarium Artium. It was formed by boiling linseed oil and amber together in the ratio of 2:1. The hardened resin acted as a non-volatile film former while linseed oil as a chemically crosslinking reactive thinner (Goldschmidt & Streitberger, 2017).

Natural products for example wood resins and vegetable oils remained as the most vital raw materials for coating production in the early 1900s. Synthetic binders such as rapid drying binders were first developed in 1920s. Use of organic solvents in coating technology has grown together with binder development. Solvents introduced in coating system aimed to accelerate drying time and optimise the application properties. Thus, wide range of solvents were produced in chemical industry globally in 1920s. Method of coating application has also evolved since 1900s. Previously, coatings were applied manually by brushing, even in the industry. Although this method is still being used now, it is only for selected few areas such as in the production of handicrafts. For industrial-scale application, modernised, mechanised, and automated application techniques are being utilised today to get higher efficiency, low material losses, qualitatively better results, and lower labour costs. Some of the innovated modern application technique include high-pressure spraying, modern automatic dipping, and electrophoretic processes as well as application by rollers.

Environmental pollution emerged and continue to become severe following the wide use of organic solvent in the coating industry. From 1960s onwards, the focus has shifted to development of environmentally friendly or low-waste coating technology. Waterborne coatings, low-solvent coatings, solvent-free powder coatings and radiation-curing coating are some of the examples of environmentally friendly coating systems. Nevertheless, solvent-containing coatings are difficult to replace without affecting quality in certain circumstances. Hence, solvent-combustion and solvent-recycling plants have been established to incinerate or recover the evaporated solvents (Goldschmidt & Streitberger, 2017; Stoye & Freitag, 2008).

2.1.2 Type of coatings

Various types of resins synthesised from wide range of raw materials have been used to produce variety of surface coatings. Some of the examples include oil-based coatings, cellulose-based coatings, vinyl coatings, acrylic coatings, alkyd coatings, polyurethane coatings, and epoxy coatings.

Oil-based coatings are prepared from natural drying oils, and they are among the oldest organic coating materials. Those coatings are usually formed through polymerisation of the drying oils. Natural drying oils such as linseed oil, tung oil and soybean oil can undergo autoxidative polymerisation in the presence of catalytic driers and atmospheric oxygen. Oil-based coatings are considered environmentally friendly coatings provided that hazardous solvents and toxic pigments are not utilised in coating formulation. They are often used to provide protection and decorative functions on coated substrates. For instance, tung oil can be applied on wood to improve its dimensional stability (He et al., 2019). Wood properties have also been enhanced by heat treatment with various vegetable oils such as linseed oil and palm oil (Dubey et al., 2012; S. H. Lee et al., 2018). The improved properties include chemical, thermal and mechanical properties, and termite and fungus resistances.

Cellulose-based coatings are generally made up of cellulose nitrate and cellulose ester. Such coatings usually require short drying time making it an excellent film-forming component. Commonly used organic cellulose ester are cellulose acetate, cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP). Cellulose acetate is the simplest organic cellulose ester that has shown outstanding properties in coating film. However, it has limited solubility and compatibility with other resins. Esterification of cellulose with blends of alkyl groups is one of the techniques that can be employed to address the abovementioned limitations. Properties of cellulose coatings can be regulated by manipulating its polymer structure and composition including hydroxyl content, chain length, and degree of substitution to suit for different applications. CABs is commonly used in metal coating industries, especially automotive coating industry to improve the metal flake orientation in the base coat that is responsible to provide metallic appearance (Edgar et al., 2001). CAP coatings have been used for drug encapsulating and drug releasing (Edgar, 2007).

Vinyl coatings are coatings formed from vinyl resins which are produced from polymerisation of monomers containing sp2 carbon unsaturation C=C. Coating materials based on vinyl resins are either physically dried or chemically cross-linked with other reactants through integration of reactive groups. One example of coating from vinyl resin is fluoropolymer coating such as polytetrafluoroethylene (PTFE). This type of coating is highly demanded in many fields since it has unique properties not shown by others, specifically its exceptional antistick and anticorrosive properties. Another example is polyvinyl alcohol which is used to produce hydrophilic capillary coatings (Belder et al. 2001). Other vinyl resins include polyethylene, polyisobutene, ethylene copolymer, polyvinyl halide, and polyvinyl ester.

The most common way to produce polyurethane coatings is by reacting di- or polyisocyanate with di- or polyol. Thermoplastic polyurethane resin is usually made from mixing stoichiometrically equal diisocyanate and diol while thermoset resin can be produced by reacting polyisocyanate and polyol with functionality greater than 2 or alternatively by using crosslinking agent. Polyurethane is widely used in coating formulation due to their excellent mechanical strength, toughness, good abrasion, corrosion and chemical resistance, and low temperature flexibility (Sridaeng et al., 2015). Polyols used to prepare polyurethane are largely derived from petroleum, however in recent years polyols obtained from renewable resources such as vegetable oils have been found to be able of partially replace the petroleum derivative (Akindoyo et al., 2016).

Vegetable oils such as cottonseed and karanja oil have been utilised to synthesise environmentally friendly polyurethane coatings (Gaikwad et al., 2015). Polyurethane coatings are widely used in various areas including coatings on metal, plastic, wood and glass materials, pipeline coating, structural and infrastructural application, automotive refinishing and large vehicle coating, such as in the shipbuilding industry (Samimi & Zarinabadi, 2012; Somarathna et al., 2018).

Resins for alkyd coatings are usually produced from esterification of polybasic acids and polyhydric alcohols. One common approach is to have the polyhydric alcohol to first undergo transesterification with vegetable oil before commencing the polycondensation with polyacid. Since alkyd resins are oil-modified or fatty-acid-modified polymers, their properties can be extensively altered by selecting different vegetable oils or fatty acids. Owing to their excellent film forming ability, easy pigmented, and ability to blend well with additives to form coatings of different characteristics, they have been widely used as coatings in various fields. For instance, alkyd resins have been utilised to prepare renewable packaging coatings which serve as moisture-protective layer (Das et al., 2021). Alkyd coatings are also utilised as furniture and architectural coatings, automotive refinishing primers, and marine coating (Aulin & Strom, 2013).

Epoxy coatings are produced from the reaction between epoxy resins and a curing agent or hardener. Epoxy resins contain epoxide groups to undergo reaction with the hardener at ambient or elevated temperature. There are variety of curing agents to react with epoxy resins, and most of them have specific functional groups that are reactive towards the epoxide groups. Advantageous properties of epoxy resins such as excellent mechanical properties, high adhesion strength, good heat resistance, and high electrical resistance make them the prime candidate to be used in various sectors. Epoxy coatings are used as protective coatings for carbon steels in electrolytic media, and aluminium materials in automobile and aerospace sectors to prevent corrosion (Verma et al., 2020).

Other than synthesis of conformal coatings, epoxy resins are also used to form intumescent coatings on steels for fire protection (Weil & Levchik, 2004).

2.1.3 Environmentally friendly coatings

2.1.3.1 Bio-based coatings

Wide selection of environmentally friendly bio-based resins available in the market today is the result from the ongoing call for global sustainable development and responsible consumption. Potential natural resources to synthesise bio-based resins are continuously being explored to replace the petroleum-based resins and produce greener coatings which can put lesser stress to the environment. Advantages of renewable raw materials which include easy accessibility and availability, more economical, and induce less environmental impact have made them an attractive resource for academical as well as for industrial research and development. Figure 2.1 shows some of the natural bio-based raw materials which are able to produce bio-based resins and thus environmentally friendly coatings.

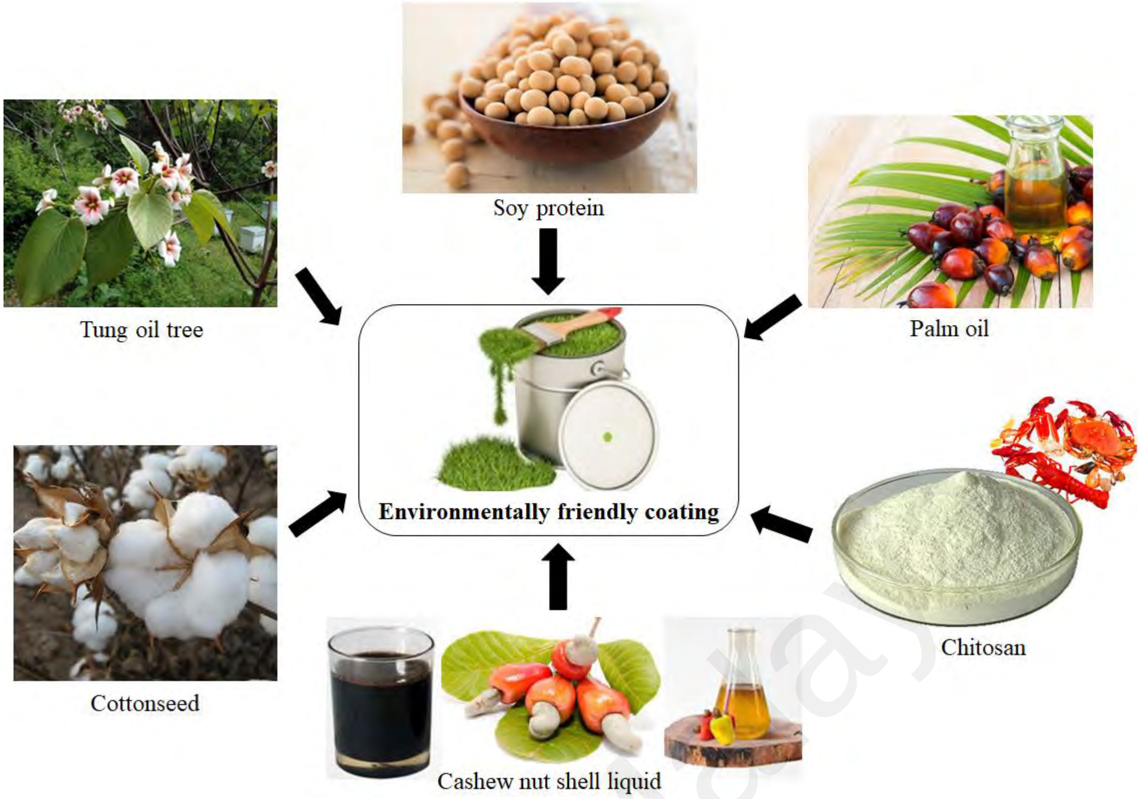


Figure 2.1: Examples of bio-based raw materials used to produce environmentally friendly coatings

Vegetable oil is one of the most important alternative natural resources to replace petroleum derivative used in coating industry. Vegetable oils has gained attention due to its relatively low cost, low toxicity, potential biodegradability, and availability. Cottonseed oil is one of the edible vegetable oils utilised in coating sector, and it is sourced from fiber plant, *Gossypium*. The crude oil is dark reddish brown in colour and is extracted from the seed of cotton. Cottonseed oil is considered a high-yield by-product from the cotton manufacturing. Cotton can be extracted and separated into two parts, which are cottonseed oil to serve as food, and cotton lint to serve as fiber crop. For each 100 kg of cotton fibers generated, there is 150 kg of cottonseeds produced with 14-23% oil content. Cotton tress grows naturally as a perennial but for commercial purpose it is grown annually (Harwood et al., 2017; Shahidi et al., 2020). Due to huge production of cotton, cottonseed oil is deemed as an accessible and sustainable natural resource for further exploitation, including for coating resin production. The oil composed of unsaturated fatty acid chains and ester groups, making it viable for reactions to take place through the double bonds and ester linkages, such as epoxidation, formation of fatty amide, formation of polyol and polymerisation (Gaikwad et al., 2015; Meshram et al., 2013a, 2013b; Narute & Palanisamy, 2016). Although cottonseed has been used more widely in biodiesel production (Aydin & Bayindir, 2010; Nabi et al., 2009; Onukwuli et al., 2017; Rashid et al., 2009; Royon et al., 2007), it has also gained traction in coating formation in last few decades. Some of the cottonseed oil-based coatings that have been reported include polyurethane coating, polyesteramide coating, and poly(ether-urethane) amide coating. There are a lot of other edible vegetable oils that have been explored and utilised in coating industry such as palm oil, soybean oil, rapeseed oil, sunflower seed oil and palm kernel oil. One of the attractive features of the oils is their availability, with record annual production of 73.49, 56.97, 27.96, 19.45 and 8.57 millon metric tons in year 2018/2019, respectively (Shahidi et al., 2020).

Tung oil is one of the traditional non-edible vegetable oils utilised in coating industry. The oil is a yellowish-brown fluid extracted from seed of tung trees, *Vernicia fordii*. The oil content of the seeds varies from 50-60%. Not only it is abundant and renewable, it has favourable characteristics that make it suitable to be exploited for coating applications (K. Huang et al., 2014; Jia et al., 2018). Pure tung oil has been used as paint and protective coating for centuries. It is a drying oil with fast self-drying ability and able to form films which are glossy, tough, hydrophobic, chemical and corrosive resistant and impermeable to water. Compositional structure of tung oil contributes to its constructive properties and accessibility towards various reactions. The oil composed of approximately 80% eleostearic acid which is a triply conjugated 18-carbon fatty acid chain, offering tung oil high amount of unsaturation. This accounts for its rapid self-drying ability and tendency to polymerise into a comprised of a complex network of crosslinked oil molecule. The unsaturated double bonds and ester linkages of tung oil also allows it to undergo various chemical reactions such as epoxidation (Jia et al., 2018), alcoholysis (Zhou et al., 2018), transesterification (Zhuang et al., 2018), hydroxylation (Mosiewicki et al., 2009), Diels Alder (Zhou et al., 2018), and Friedel Crafts (Zhou et al., 2016).

Man et al. reported the use of tung oil-based derivative in the formulation of multifunctional eco-friendly coatings. They revealed that film properties of the coatings improved significantly with the increase of tung oil-based polyol content. Besides enhancing the thermal property, mechanical property, hydrophobicity and water absorption property, the coatings showed positive antibacterial property as well (Man et al., 2019). Tung oil has been reported to serve as healing and lubricating agents in synthesis of self-healing and self-lubricating epoxy coatings (Li et al., 2018; Samadzadeh et al., 2011). The tung oil serve as oxidative healing agent and provides repairing for coatings through in-situ polymerisation. Such self-healing properties prevents the substrate underneath from encountering moisture and subsequently prevent corrosion from taking place. According to the work done by Liang et al., UV-curable coatings formulated from tung oil-based derivative possessed outstanding hardness, high glossiness and excellent water resistance (Liang et al., 2019). Tung oil is also utilised in the production of alkyd coatings as part of alkyd resins (Thanamongkollit et al., 2012) or as reactive diluent for alkyd resins (Biermann et al., 2010). The reduction of organic solvent used as reactive diluent by replacing with renewable reactive diluent contributed to reduced emission of volatile organic compounds. Another desirable property of tung oil-based coating that benefits the environment shown is its biodegradability, as reported by Yang et al. (Yang et al., 2015).

Another outstanding natural raw material that has been used to substitute petroleum-based raw materials in coating industry is cashew nut shell liquid (CNSL). CNSL is found in the shells of cashew fruits of cashew trees, *Anacardium occidentale* and it appears as reddish brown viscous fluid. Large production of cashew nut makes CNSL a continuous source available as natural raw materials. Other than its availability and sustainability, being an agricultural by-product from cashew nut production, CNSL is cost effective. In respect of performance, extracted CNSL contains a variety of versatile phenolic derivatives with saturated or unsaturated long hydrocarbon chains. This allows them to undergo various polymerisation reactions involving addition or condensation mechanism. The existence of aromatic ring and long hydrocarbon chains contributes to the good balance between flexibility and hardness of coatings (Balgude & Sabnis, 2014). Thus, they are widely used in a number of industrial applications which include various paint and coating resins. Previous research done by Kim et al. reported that a glossy transparent film with outstanding hardness was formed after the curing of epoxide-containing polycardanol derived from CNSL and phenalkamine (Kim et al., 2007). A series of crosslinked polyurethanes synthesised from a derivative of CNSL reported by Mythili et al. shown good thermal stability and mechanical strength (Mythili et al., 2005).

Chitosan is a polysaccharide sourced from chitin, which is one of the most abundant polysaccharides in nature. It is derived from chitin by heterogeneous deacetylation and consists of (1,4)-linked-2-amino-deoxy-β-D-glucan (Deepthi et al., 2016). Chitosan molecule is a copolymer of N-acetyl glucosamine and glucosamine, and it can be obtained from microorganisms, fungi, and the shells of crustaceans (Vazquez et al., 2013). Chitosan is widely used as natural bioactive biopolymer as it is non-toxic, exhibits antimicrobial and antifungal properties, biocompatible, biodegradable and has excellent film forming property. Chitosan has gained attention to serve as biomaterial in medical field (Dash et al., 2011). De Campos et al. reported the development of chitosan-coated nanocapsules to interact with corneal epithelium and act as ocular drug carriers (De Campos et al., 2003). D'Almeida et al. revealed that chitosan-based coating has potential of forming antibacterial surface to prevent implant related infections (D'Almeida et al., 2017). Chitosan is also widely used in food preservation since it forms edible semi permeable film to serve as a safer alternative to chemical preservatives. Chitosan-based coatings are applied on meats, vegetables, and fruits to maintain their qualities, enhance storability and prolong shelf life. Previous researches revealed that chitosan-based coatings help to inhibit melanosis on seafood (Yuan et al., 2016) and delay microbial growth on cooked meat under cold storage condition (Yingyuad et al., 2006). The coatings are also proven to preserve fruits effectively by retaining fruit surface moisture and reduce juice leakage (Dong et al., 2004). El Ghaouth et al. showed that the chitosan's antifungal effectiveness on fresh fruit was comparable with fungicide. Bhale et al. coated eggs with low, medium and high molecular weight chitosan and they revealed that the interior quality of chitosan-coated eggs was effectively preserved up to 3 weeks longer compared to non-coated eggs (Bhale et al., 2003).

Lignin is one of the representative fiber-based bio-resources utilised in coating industry. It is one of the most abundant natural polymers. Lignin forms part of the secondary cell walls of plants to impart the strength and rigidity to plants. Lignin contributes about 30 % of the dry weight of softwoods and approximately 20% for hardwood. Its compositional structure has great diversity depending on its origin (Calvo-Flores & Dobado, 2010). In general, backbone of lignin composes phenylpropane units linked together by different bonds. Lignin is a by-product in vast amount resulting from the wood delignification process in pulp and paper industry. The properties of lignin also vary according to the delignification process. Besides renewability and availability of lignin, its non-toxic, environmentally compatible, hydrophilic properties and biodegradability has attracted the interest of many to utilise it in coating formulation.

Reaction sites for further functionalisation include the substituted methoxyl groups, phenolic and aliphatic hydroxyl groups (Hatakeyama & Hatakeyama, 2010; Hult et al., 2013). Hult et al. reported the potential of lignin-based coating to serve as sustainable barrier material for paper boards and to replace the petroleum-based barrier materials. Mulder et al. and Li et al. reported the successful formulation of lignin-based controlled release coatings and the improvement in monitoring the releasing rate of fertilisers (J. Li et al., 2017; Mulder et al., 2011). According to previous studies, lignin coating was also reported as an excellent anticorrosive coating on steel substrate (Dastpak et al., 2018; Ding et al., 2016). Other than that, lignin was utilised to formulate coatings for repairing (Hao et al., 2019) and antifouling (Shamaei et al., 2020) purposes.

Despite the advantages of bio-based coatings, there are some drawbacks need to be taken into concern during the synthesis of bio-based coatings such as the availability and characteristic of renewable materials. The availability of natural resourced-materials especially those obtained from plants could be less stable due to weather, natural disaster and seasonal nature. The processing and extraction procedure for bio-based materials come from both plants and animals could be complicated and tedious. Other than that, the nature properties of bio-based materials which could affect the performance of surface coatings produced are needed to be overcome in order to turn them into a valuable coatings such as poor mechanical strength, moisture sensitivity, gas permeability and so on (Jabeen et al., 2015; Ribba et al., 2017; Vinod et al., 2020).

2.1.3.2 Green technologies and curing methods

Other than introducing renewable raw materials in coating production line, implementing green technologies in formulation process and/ or curing of coatings is another aspect of an environmentally friendly coating.

Waterborne coatings were first developed in the 1950s, and they are considered as one of the green coatings since water is used as solvent or diluent to replace the combustible and toxic organic solvent (Stoye & Freitag, 2008). There are three principal types of waterborne coatings, which are water-soluble, water-dispersible, and emulsion (Williams & Randall, 1994). Water-soluble coatings comprise of water-soluble resins which can be fully dissolved in water. The resins are generally produced through polycondensation reactions in an organic medium. Thus, majority of them contain organic co-solvents that are soluble or miscible with water. The conventional resins involved are polyesters, polyacrylates, alkyds, and epoxies. Water-dispersible coatings consist of suspended small insoluble resin particles in water. Suspension is achieved via high-shear mechanical agitation. Organic solvents are used as coalescing agents in small amounts, and they can be evaporated through drying. Typical resins include vinyl propionate, acrylate-methacrylate, vinyl acetate and styrene-butadiene polymers. As for emulsion waterborne coatings, emulsifiers are normally required to maintain the clusters in suspension as the resin clusters tend to be larger than those in water-dispersible coatings (Javadi et al., 2020).

Water has high boiling point and high latent heat of evaporation. This causes the low evaporation rate of water and relatively longer time is required for films to dry. High surface tension of water results with insufficient wetting, unsatisfactory edge covering and formation of crater on substrates with low critical surface tension. Pre-treatment of substrates are often needed to overcome this problem. Another disadvantage of waterborne coatings implementation is the equipment used in production and storage of the coatings must be corrosion resistant, and this will incur additional cost. As for the advantages, other than low toxicity, waterborne formulations often comprise of only minimal content of volatile organic compounds (if any), less odour, less flammable, reduced hazardous waste disposals, and containers or reactors can be easily cleaned with water or water-based cleaners (Weiss, 1997). Due to the absence or low content of organic solvent, waterborne coatings are deemed as less harmful to the environment compared to the corresponding solvent based coatings. They are currently being utilised in various sectors including in architectural, wood, automotive, coil and packaging sectors.

Powder coatings were first made available in the 1950s. They are 100% solids coatings which was formulated without any liquid solvent. There are two primary type of powder coating systems which are thermoplastic and thermosetting systems. Thermoplastic powder coatings are made up from thermoplastic resin, pigment, filler, plasticiser and stabiliser, whereas thermosetting powder coatings are made of thermosetting resin, curing agent, pigment, filler, and additives. Resins of thermoplastic coatings include polyethylene, polyamide, polyvinyl chloride, and polyvinylidene fluoride. The thermosetting coatings are generally formulated from epoxy resin, polyester resin and acrylic resin along with various hardeners. Films of powder coatings derived from different type of resins exhibit different properties. For instance, epoxy resin powder coatings exhibit outstanding corrosion resistance, hardness, flexibility, and impact strength. Acrylic resin powder coatings show good weather resistance, pollution resistance, colour retention and excellent metal adhesion. Polyethylene powder coatings have good electrical insulation and excellent corrosion resistance. The coating components are extruded, crushed and screened into fine powder which is then stored at room temperature. Powder coatings are manufactured by dry process production and wet process production. Dry process includes dry mixing, melt mixing and supercritical fluid methods, while wet process production involves evaporation, precipitation and spray drying methods. Powder coatings typically operated by electrostatic spraying method for thermoset powder coatings and fluidized bed dipping method for thermoplastic powder coatings. The powder coated substrate is then heated to melt and cure the powder into film (Du et al., 2016).

Disadvantages of this technology include high bake temperatures that cause coating of large and complex objects to be difficult, limited colour changeability and potential of forming explosive powder-air mixtures in certain concentration range. Nevertheless, the explosion risk is considerably lower than that of solvent-based coatings. Advantages of powder coatings include the use of minimal or no volatile organic content, high application efficiency, energy savings, durable finishes and elimination of hazardous waste. In contrast to wet materials, almost no material is lost during application of powder coatings. This is because any spilled powder during application can be easily retrieved and reused. Powder coatings are applied on pipe and wire articles, building and construction industry, automotive sector, and appliances sector. Powder coatings is one of the most environmentally friendly coatings since there is no waste generated, solvent-free, separation of dust-air mixtures is simple, and do not contain volatile hazardous components.

Radiation curing is a technology that cure films by mean of electromagnetic radiation such as ultraviolet, visible, and infrared light or by mean of ionising radiation, such as electron beam. Both types of radiations initiate the chain reactions in resins and turn them into cross-linked polymer networks and tack-free films. The main components in UV-curable coating formulation include prepolymers, monomers, photoinitiators, and additives. Prepolymers are oligomer resins such as acrylated epoxy, acrylated polyester, acrylated urethane and acrylated oil, and the properties of the films produced could vary significantly. For instance, acrylated epoxy resins usually produce hard, solvent-resistant films with fast cure, whereas acrylated urethanes show excellent film flexibility and toughness. As oligomers have relatively high viscosity, monomers which are also referred to as reactive diluents are used to replace solvent and dilute the oligomers down to applicable viscosities. Reactive diluents must be crosslinkable and are integrated into the network during crosslinking, thus influence the physical and chemical properties of the coatings. Photoinitiator is a light sensitive compound that can absorb light energy and produces reactive species which are responsible to initiate polymerisation of oligomeric binder into a hard solid mass. There are two types of photointiators, those that generate radicals by intermolecular abstraction of hydrogen, or those that produces radicals by intramolecular photocleavage. Curing process involves initiation, propagation and termination steps. The principles of formulation and curing of ionising radiation curable coatings (electron-beam curing) are majorly similar to the UV curable coatings. There is however a difference in the initiation step, specifically the way radicals are generated in the two systems. Radicals in UV curing coatings are produced through chemical decomposition of photoinitiators while in an electron-beam curing system, radicals are produced by interaction of accelerated electrons with organic compounds, which is usually the polymeric binder. As for curing equipment, mercury or electrodeless gas-filled UV lamps are normally used for electromagnetic radiation, while scanner type or linear cathode type electron beam accelerators are required for ionising radiation (Sharmin et al., 2015; Shukla et al., 2004).

Disadvantages of radiation curable coatings include premature polymerisation and tendency of film shrinkage which could affect the film adhesion. The advantages however includes formulation that is free of volatile organic solvent, rapid curing at ambient temperatures, minimum substrates heating that allows application on thermal sensitive substrates, reduced process time due to high curing efficiency, simple to operate, and requires minimal floor space (Williams & Randall, 1994). Radiation curable coatings are widely used on plastics, paper, wood, metal containers, electronic components and flooring (Stoye & Freitag, 2008). Such coatings are deemed as clean and green as no volatile organic compounds is emitted during coating formation.

2.1.4 Function of coatings

Coatings are applied on substrate to serve various functions and purposes, and this primarily includes protective and decorative functions. There are however coatings that were applied to serve certain specific functions such electrically conductive coating and flame retardant coating.

Electrically conductive coatings are applied on insulating substrates to derive the electrical conductivity of the coated articles. There are four types of conductive coatings, namely metallic, filled polymer, polymeric, and organometallic conductive coatings (Tracton, 2005). Common commercial metallic coatings include nickel, copper, palladium, platinum, silver, zinc, chromium, gold, cadmium, tin, and lead. Metallic coatings are generally use to metallised plastics by means of metal spraying, electroless plating, and vacuum metallisation. As for filled polymeric conductive coatings, plastic coatings can be made conductive by adding metallic fillers. There are some polymeric conductive coating that does not requires metallic filler, but such coating are those that comprised of molecularly conductive polymeric particles. Organometallic conductive coatings are prepared from metal containing polymers. The most common application of conductive coatings is to provide electroactivity for electronic and optoelectronic devices (Jin et al., 2017; Lam et al., 2018). Conductive coatings are applied on photoelectodes to prevent photocorrosion (Kim & Yang, 2019). They are also used in metallisation of waveguides (Tak et al., 2017) and prevention for penetration loss of waves (Huang et al., 2021). Other than that, electrically conductive polymeric materials are utilised in formulating the matrices of aircraft composite structures to provide damage protection from lightning strike (Katunin et al., 2017).

Fire-retardant coatings are formulated to retard combustion by preventing the spreading of flame via various mechanisms. Some of the commonly used fire-retardant additives in coatings are antimony oxide, triaryl phosphate ester, alumina trihydrate and magnesium hydroxide. These additives tend to terminate the combustion by different ways such as by shielding or insulating substrate from flame and heat, absorption of heat by decomposition, or releasing large amount of water by hydration. Fire-resistive intumescent coatings form physical barrier to prevent or minimise heat transfer from the flame to the substrate, and the key components in such coating include carbonific compound, acid releasing agent, and spumific compound (Gu et al., 2007; Tracton, 2005). Intumescent coatings swell and char when exposed to flame and high heat, where a carbonaceous foam is formed to insulate the coated substrate from heat, oxygen, and fire, and subsequently delay the onset of combustion of substrates. Fire-retardant coatings are usually applied on flammable substrates such as woods, textiles and plastics as well as torsional substrates such as steels to reduce the fire hazard in various fields (Chou et al., 2009; Hu et al., 2019; Weil & Levchik, 2008; Williams et al., 2020)

Coatings play an important role in corrosion control, and they are often applied on substrates to prevent corrosion. There are three types of coatings utilised in corrosion control, which are barrier coatings, inhibitive coatings and zinc-rich coatings. Barrier coatings forms impermeable barrier coatings to suppress the transmission of oxygen and ionic solutions up to an extent that corrosion could be avoided (Sorensen et al., 2009). They are generally used for extreme condition such as the lining of water, food, fuel, and chemical storage tanks, as well as marine coatings. Inhibitive coatings made up from inhibitive pigments which is responsible to reduce the corrosion through chemical modification on the interfacial environment against metal surfaces. They are commonly used for light to moderate duty atmospheric condition and also in some high-performance systems such as aircraft coatings, automotive primers and coil coating primers. In general, they are not preferred for application that involves long term freshwater immersion. Zinc-rich coatings made up from large amount of zinc dust pigments. They preclude occurrence of corrosion galvanically by acting as the anode of an electrochemical cell which itself corrodes sacrificially to protect the steel (Tracton, 2005). Zinc-rich coatings are usually used in neutral environments.

Exterior wood coatings are applied to protect wood surface, maintain their appearance and offer cleanability. Wood coatings are usually oil-based finish, most commonly from linseed and tung oil derivatives (Humar & Lesar, 2013; Peng et al., 2021). Woods exposed outdoors undergo physical and chemical changes due to exposure to sunlight, fluctuating temperature, moisture and bacterial attack. These cause changes in molecular structure, surface deformation, cracking, discolouration and erosion of the woods (Nejad & Cooper, 2017). To provide protection, exterior wood coatings are usually applied to block the damaging ultraviolet light and shield the woods from moisture (Ozgenc et al., 2012; Tracton, 2005).

There are many other specific functions that coatings could offer. For instance, optical fiber coatings are usually applied to preserve the optical fiber's strength and at the same time protect the fiber from lateral deformation, thus avoid undesired reduction in transmitting light signal. Pharmaceutical tablet coatings are utilised to improve drug stability by protecting the drug from oxygen, moisture, and light that could degrade the drug. Coating of tablets is also purposed for regulating the duration and site of drug release. For leather coatings, tanned leathers are generally coated with pigmented or lacquer coatings for aesthetic purpose as well as to protect the articles from water and air. Marine coatings provide protection of the underwater surfaces of deep-sea ships, offshore platforms, and pleasure crafts from the fouling and growth of marine organisms such as fungi and algae.

2.2 Epoxy coating

2.2.1 Background

Epoxy resins indicate the low-molecular-weight prepolymers that contain more than one reactive epoxy groups which is capable to be converted into thermoset polymer after curing (Takeichi & Furukawa, 2012). According to rigorous definition, epoxy resins denote only the uncrosslinked monomers or oligomers comprising epoxy groups. Nevertheless, the term “epoxy resins” is used to refer the cured epoxy systems in practice at times. It is noteworthy that cured epoxy resins possess very little or no epoxide groups.

The first attempt on preparing the epoxy resin was in 1891 by reacting epichlorohydrin with 1, 2-dihydroxybenzne, an aromatic polyglycidyl ether was formed and it was not known as epoxy resin at that moment. The first patent recounting the polyglycidyl ether was recorded in year of 1933 (Dearborn et al., 1953). They are recognised as “epoxy resins” when marketing the commercial epoxy resins that were synthesised from the independent works of Pierre Castan in Switzerland and Sylvan Greenlee in United States in 1940s (Ellis, 1993). Greenlee produced resins with a relatively higher molecular weight in order to develop superior surface coatings. These resins were prepared by reacting the bisphenol A and epichlorohydrin, by reacting with drying oil fatty acids, alkyd-type epoxy ester coatings were produced and marketed through the subsidiary Jones-Dabney Co. (Pham & Marks, 1991). The epoxy coatings synthesised by Greenlee exhibited enhanced adhesion, hardness, inertness and thermal resistance compared with alkyd or phenolic resins. Since the first commercialisation of diglycidyl ether of bisphenol A (DGEBA) resins in the 1940s, epoxy resins have gradually established their position as a key category in industrial polymers.

Development of innovating the epoxy resins involves the synthesis of epoxy resins with specific characteristics. Another vital material in the curing of epoxy resin to turn them into applicable form is hardener (Mohan, 2013). Thus, it is equally important to develop various type of hardeners which may vary in reactivity with epoxy groups. With the aim of easing processing as well as amending cured resin properties, other components may be introduced which include solvents, diluents, fillers, catalysts, accelerators, plasticizers, and tougheners. Other than curing agents and additives, the final properties of cured epoxy resins are also affected by the curing mechanism, degree of curing, number of functional groups in resins and hardeners, ratio of resins and hardeners, as well as molecular structure of bridges between functional groups in resins and hardeners.

Common commercial epoxy resins include diglycidyl ether bisphenol A (DGBEA), diglycidyl ether bisphenol F (DGBEF), and epoxyphenol novolac (EPN) which are formed by reacting epichlorohydrin with different materials such as bisphenol A, novolac, aliphatic epoxy resins, halogenated epoxy resins and so on. Thus, providing various properties to epoxy resins include corrosion resistance, high thermal stability, high mechanical strength, high chemical resistance, durability, and adhesion. Owing to these properties, epoxy resins find application in diverse sectors such as paints and coatings, adhesives, electronic encapsulation, automotive and composites (Gardiner et al., 1992). With the outstanding performance properties, excellent formulating versatility and reasonable coats, they gain high demand in application for various sectors especially protective surface coatings which have been the first major commercial application of epoxy resins, and they continue to remain as a main outlet for epoxy resin consumption. However, the demand of biodegradable polymers in recent year defer the growth of epoxy resin demand in future as most of the epoxy resins available in market are petroleum derivatives.

2.2.1.1 Epoxy resins

(a) Characteristics of epoxy resins

Epoxy resins are low molar mass prepolymers containing epoxide end groups which appear in liquid state as well as solid state. Some of the advantageous properties of liquid epoxy resin include:

- **Relatively lower viscosity**: liquid resins produce epoxy systems with lower viscosity than the high-molecular-weight solid resins which able to facilitate modification and processing.
- **Easy cure**: epoxy resins can be cured at ambient and elevated temperature quickly. Curing temperature is depended on the curing agent selected.
- **Low shrinkage**: there is low shrinkage occurred during the cure. Epoxy resins react with curing agent without releasing volatile by products.
- **High adhesive strength**: epoxy resins possess outstanding adhesion ability due to the presence of polar hydroxyl and ether groups. Surface contacts between the resins and substrates are not affected and remained as possible as it is since shrinkage is low while curing.
- **Good chemical resistance**: chemical resistance of cured epoxy resins affected substantially by the curing agent chosen. In general, majority epoxy resins exhibit extremely high resistance to alkali and good resistance to acid.
- **High mechanical properties**: well-formulated epoxy resins typically exhibit relatively higher mechanical strength than other type of resins.
- **Versatility**: the characteristics of epoxy resin may be modified in various ways: blending of resin types, selection of curing agents, and addition of modifiers and fillers.

Liquid epoxy resins are commonly applied in coatings, flooring and composites formulations since their low viscosity form easy-to-process systems. Large amount of liquid epoxy resins are utilised as starting materials to produce higher molecular weight solid epoxy resins, and converted to epoxy derivatives, for instance, epoxy vinyl esters, epoxy acrylates and so on.

High-molecular-weight solid epoxy resins are widely used in coatings industry especially solution coatings. The epoxy resin backbone renders toughness, chemical resistance, and scratch resistance. The longer backbones offer greater distancing between crosslinks when crosslinking via the terminal epoxy groups, give rise to improved flexibility and toughness. The outstanding adhesion, mechanical strength, simplicity of cure, and high chemical resistance are also the vital advantages of the solid epoxy resins as the liquid epoxy resins (Takeichi & Furukawa, 2012).

(b) Synthesis of epoxide groups

The parent compound ethylene oxide, or oxirane was first produced by Wurtz. It is synthesised from reaction of ethylene chlorohydrin with aqueous alkali, this method was published in 1859 by Wurtz. Figure 2.2 show the synthesis of ethylene oxide. This process is general for the synthesis of epoxy compounds, however ethylene oxide is more commonly prepared by other methods nowadays such as direct oxidation of ethylene with air or oxygen and a silver catalyst.

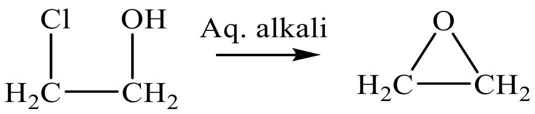


Figure 2.2: Synthesis of ethylene oxide

There are a lot of methods to synthesise epoxy rings established which attributed to the successive studies of various chemists. The important ways for the manufacture of epoxy resins typically include the reaction of halohydrin with hydroxyl compounds and the oxidation of unsaturated compounds with a peracids.

(c) Synthesis of epoxy resins

Epichlorohydrin is a versatile oxirane-containing compound that widely used for the production of epoxy resins. Epichlorohydrin form epoxy resins by react their epoxide groups with multifunctional phenols, halogenated phenols, multifunctional alcohols, novolacs, carboxylic and fatty acids, and amine compounds. The reaction between epoxide groups and hydroxylic compounds happens readily in the presence of an alkali catalyst, then a new epoxy ring is formed through dehydrohalogenation (Ellis, 1993). The proposed route is presented in Figure 2.3.

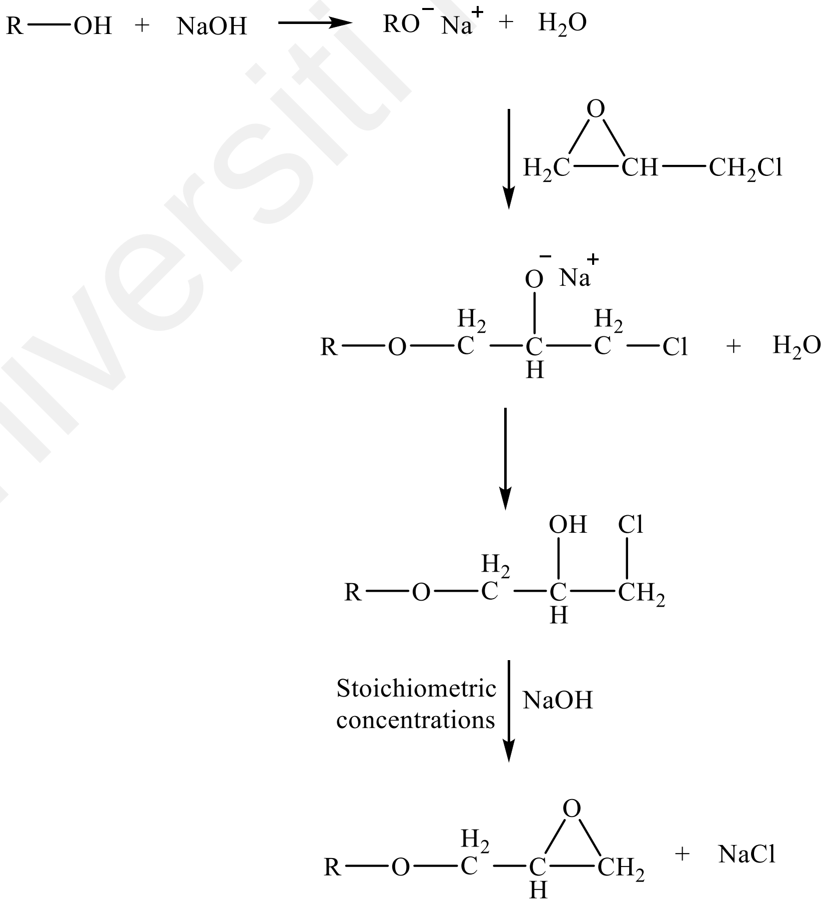
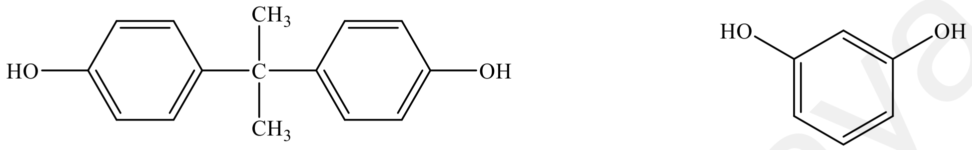


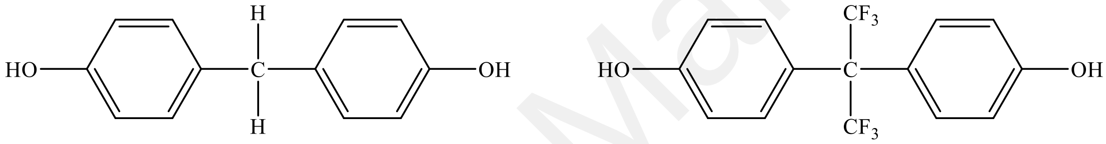
Figure 2.3: Reaction of epichlorohydrin with hydroxylic compound

The multifunctional hydroxylic compounds are determined as major precursors for the synthesis of epoxy resins, whereas some monofunctional hydroxylic compounds are used for the manufacture of resin modifiers. Phenols account a large group of the precursors, some of the general phenols utilised in production of epoxy resins shown in Figure 2.4.



Bisphenol A

Resorcinol



Bisphenol F

4,4'-(perfluoropropane-2,2-diyl)diphenol

Figure 2.4: Common phenols used for the synthesis of epoxy resins

Epoxy resins can be categorised into different class according to their structures and element carried which lead to vary properties. Several type of epoxy resins are listed in Table 2.1.

Table 2.1: Type of epoxy resins

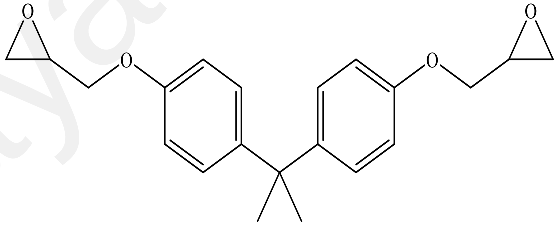
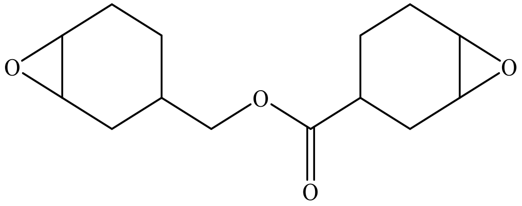
Type of epoxy resin	Properties	Application	Synthesis	Example
Bisphenol A epoxy resin	Rigidity, strength properties, excellent chemical and mechanical properties (Nikafshar et al., 2017)	Engineering applications (Kumar et al., 2018)	Reaction between epichlorohydrin and bisphenol A in presence of a basic catalyst such as sodium hydroxide (Takeichi & Furukawa, 2012)	 bisphenol A diglycidyl ether
Cycloaliphatic epoxy resins	Outstanding UV stability, good thermal stability, and excellent electrical properties (Yoo et al., 2010)	Coating and electronic industry (Tao et al., 2007)	Reaction between 3'-cyclohexenylmethyl 3-cyclohexenecarboxylate and peracetic acid (Jin et al., 2015)	 3',4'-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate

Table 2.1, continued.

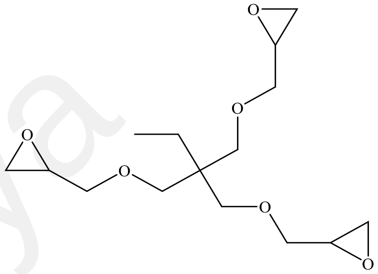
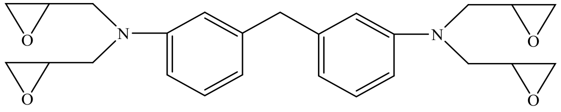
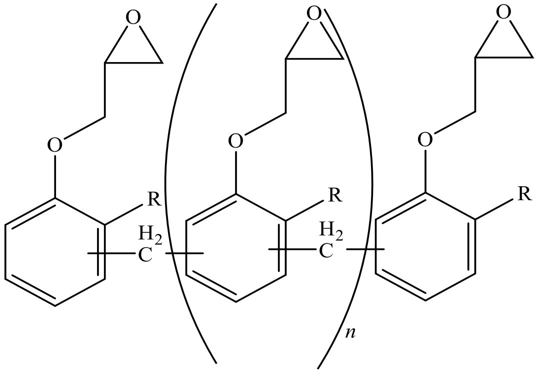
Multifunctional epoxy resins	Enhanced thermal, mechanical, and adhesion properties due to highly crosslinked structure (Pham & Marks, 1991)	Military and civilian applications (Mustata & Bicu, 2000)	-Reaction between trimethylol propane with epichlorohydrin 1,3-diaminobenzene or 4,4'-aminodiphenyl methane. -Reaction between epichlorohydrin with multifunctional amine compounds (Jin et al., 2015)	 trimethylolpropane triglycidyl ether  *N*,*N*,*N*′,*N*′-tetraglycidyl-4,4'-diaminodiphenylmethane
Novolac epoxy resins	Improved thermal stability, excellent chemical and solvent resistant properties, and good adhesive property (Park et al., 2000)	Chemical process equipment such as storage tanks, liners for pumps, corrosion-resistant coatings, aerospace composites (Pham & Marks, 1991)	Condensation of phenol and formaldehyde with presence of acid catalyst forms phenol novolac, followed by epoxidation of the novolac with epichlorohydrin (Pham & Marks, 1991)	 Phenol novolac resins , R=H Cresol novolac resins , R=CH_3

Table 2.1, continued.

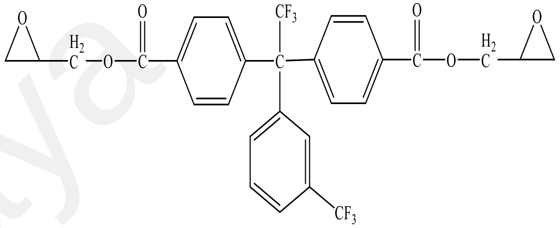
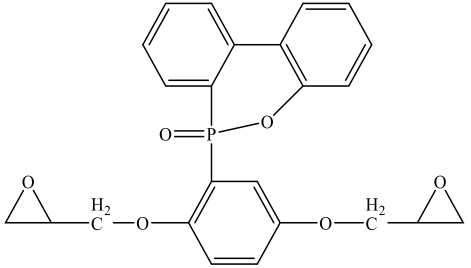
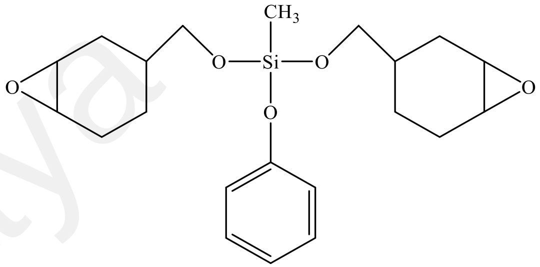
Fluorine-containing epoxy resins	Excellent chemical resistance, relatively lower water absorption, and improved electrical insulating property (Tao et al., 2007)	High performance applications, including specialty coatings and composites such as anticorrosion coatings (Pham & Marks, 1991)	Implementing fluorinated monomers or oligomers such as hexafluorobisphenol A (Pham & Marks, 1991)	 1,1-bis(4-glycidylesterphenyl)-1-(3'-trifluoromethylphenyl)-2,2,2-trifluoro-ethane
Phosphorus-containing epoxy resins	Improved flame retardant, and thermal stability (Wang & Shieh, 1999)	Electronic encapsulation which require character of flame retardant effectiveness (Mohan, 2013)	Integrating covalently-bonded phosphorus into epoxy resins using phosphorus-containing oxirane compounds (Jin et al., 2015)	 6-H-dibenz[c,e][1,2] oxaphosphorin-6-[2,5-bis (oxiranylmethoxy) phenyl]-6-oxide

Table 2.1, continued.

Silicon-containing epoxy resins	Good thermal stability and mechanical properties (Liu et al., 2012)	Electrical application such as light-emitting diodes encapsulation (Yang et al., 2011)	-Hydrosilylation reactions between unsaturated epoxy compounds with siloxanes (Crivello & Bi, 1993) -Condensation of hydroxyl-terminated siloxanes with epoxy compounds such as epichlorohydrin and DGEBA -Catalytic transetherification between alkoxysilane and glycidol (Mercado et al., 2006)	

2.2.1.2 Curing agents

Conversion of epoxy resin into hard thermoset with highly crosslinked three dimensional network is accomplished by addition of curing agents. Curing agents also called crosslinkers, hardeners, and activators. Some of them catalytically promote crosslinking, and others take part directly in the reaction and chemically bound into the resin. Epoxy resins can be cured by homopolymerisations initiated by catalytic curing agents to form homo epoxy polymers; or through polyaddition/ copolymerisation reactions with a multifunctional curing agents to produce hetero polymers made up from epoxy resins and curing agents (Takeichi & Furukawa, 2012). There are also mixture products of both type of curing process. Initially there are relatively few typical types of curing agents are recognised, these include simple amines, acid anhydrides, phenol-formaldehyde and amino-formaldehyde resins. The choice of curing agents are extended and multiplied such as polyfunctional amines, polybasic carboxylic acids, mercaptans and even inorganic chemicals. This is because alternative types of epoxy resin are developed as well as application development for epoxy systems, thus modified curing agents are needed to fulfil specific ultimate requirements (Ashcroft, 1993). Examples of the curing agents for epoxy resins are shown in Table 2.2.

Table 2.2: Curing agents for epoxy resins

Class of curing agent	Description	Examples of curing agent	Advantage(s)	Disadvantage(s)
Nitrogen-containing curing agent	Functionality of amine curing agent is determined by number of hydrogen atoms bonded to nitrogen atom. Primary amine comprised of two amine hydrogens able to react with two epoxy groups whereas a secondary amine reacts with only one epoxy group. Tertiary amine group has no active hydrogen does not react readily with epoxy group, is rarely used solely as a curing agent yet it act as an accelerator/ catalyst to speed up epoxy reaction. 1˚ amines have been reported able to react with epoxy resins in higher rate than 2˚ amines.	Aliphatic amines	Relatively low viscosity, cure at ambient temperature, excellent chemical resistance and solvent resistance.	Short pot life, critical mix ratio with epoxy resins, high moisture absorption due to hygroscopic property, risk of blush and carbonation, and limited flexibility.
		Cycloaliphatic amines	Relatively low viscosity, long pot-life, offer ambient and elevated temperature curing, good electrical property, improved thermal and mechanical properties compared to aliphatic amine, adhesive property to wet cement, and relatively low toxicity.	Lower reactivity rate, and high cost.

Table 2.2, continued.

Aromatic amines	Long pot life, better chemical resistance and higher thermal resistance than curing with aliphatic and cycloaliphatic amines, and low moisture absorption.	Preheating is needed to melt the solid amine, warming epoxy resins is needed to enhance solubility, long cure cycles at high temperature, and toxicity.
Polyamides	Afford mild condition curing, good intercoat adhesion, excellent concrete wetting, goo moisture resistance, and low toxicity.	Lower curing rate, darker colour formed compared to polyamine-cured epoxies, and limited use in elevated temperature applications.
Amidoamines	Significantly lower viscosity, good toughness, improved flexibility, and better moisture resistance than aliphatic polyamines.	Poor performance at high temperature.

Table 2.2, continued.

Oxygen-containing curing agent	Carboxylic acid functional polyesters and anhydrides are majorly practical in heat-cured applications, such as surface coatings and stoving enamels Polyesters have grown significantly in polyester–epoxy hybrid powder coatings. Anhydrides have well replaced the relatively more toxic aromatic amines in composites. Phenolic compounds include phenol-, cresol-, and bisphenol A terminated epoxy resin hardener, phenolic resole and novolacs are reactive with epoxy groups. Reactions between amino-formaldehyde resins with epoxy resins at elevated temperature (normally ≥ 150°C) yield products with more extensively crosslinked networks compared to phenol-formaldehyde cured epoxy resins.	Carboxylic-terminated polyesters	Good corrosion resistance, weatherability, and mechanical property.	Poor chemical resistance
		Acid anhydrides	Good thermal, mechanical and electrical properties, low shrinkage and viscosity, and long pot life.	Long cure cycles at high temperature.
		Phenol–formaldehyde novolacs	Good chemical resistance, electrical properties, shelf stability, and high thermal resistance.	Elevated temperature curing, and poor UV stability.
		Phenol–formaldehyde resoles	Excellent chemical resistance.	High temperature curing, and brittle.
		Melamine–formaldehyde	Superior film hardness and gloss properties.	High temperature cure.

Table 2.2, continued.

Sulphur-containing curing agent	The thiol or mercaptan group (SH) alone reacts slowly with epoxy resins at ambient temperature. Amines are used as initiator/ co-curing agents to promote rapid curing time. When thiol groups are converted by amines to mercaptide ions, they becomes extremely reactive.	Polysulfides and polymercaptans	Rapid curing time at ambient temperature and excellent adhesion property.	Poor performance at high temperature, and displeasing odour.
Catalytic curing agent	Catalytic curing agents are not being integrated into the cured polymer networks. They promote crosslinking by homopolymerisation, function as accelerators, co-curing agents as well as activators. Some remain inert under ambient temperature and indoor lighting, become active by introducing external stimulation, such as heating or photo irradiation.	Imidazole	Effective cure at relatively low temperature especially those with high basicity, and good thermal properties.	
		Tertiary amine	Effective cure at room temperature.	

2.2.1.3 Additives and modifiers

In addition to the two main components of epoxy formulations, which are resins and curing agents, various other materials could be introduced into epoxy systems to modify and amend the desired properties of uncured and cured epoxies. Common additives or modifiers include diluents, fillers, plasticisers, toughening agents, and thixotropic agents. Some materials carry more than one modifying functions into epoxy systems.

Solvents and diluents

Solvents are an important additives for surface coating. Solvents are introduced either in single type of solvents or in blends of various solvents to attain higher magnitude of solvating power. Selection of suitable solvents takes account into a few factors. The factors are solvating power and evaporation rate of solvents, cost, and safety. Solvent power and evaporation rate intensely affect the viscosity and the ultimate properties of surface coatings. Examples of solvents include toluene, tetrahydrofuran, methyl ethyl ketone, 2-ethoxyethanol, xylene, and 2-ethoxyethyl acetate.

Diluents are employed with purpose of reducing viscosity in the formulation. Consequently, aiding general processability as well as increasing the extent of incorporation of other additive components. Diluents are also added with intend of improving the characteristics of epoxy systems such as wetting. Diluents can be classified into two categories which are reactive and non-reactive types.

Addition of non-reactive diluents at certain level could increase the extent and/or rate of curing. However, high concentrations of non-reactive diluents result in deterioration on the properties of cured epoxy, due to the presence of voids in the cured resins caused by their non-reactivity (Shaw, 1993; Pham & Marks, 1991). Examples of non-reactive diluents are toluene, xylene, dibutyl phthalate, styrene and various phenolic compounds.

Reactive diluents can be divided into epoxy-containing diluents and non-epoxy based reactive diluents. There are two classes of epoxy based reactive diluents; monoepoxy compounds and di/polyfunctional epoxies. Both classes comprise of epoxide groups that allows the diluent to participate polymerisation and crosslinking reaction with the resins and curing agents, hence diluents are chemically bound into the crosslinked network (Shaw, 1993). Non-epoxy based reactive diluents which derive their reactivity from functional groups other than epoxide include triphenyl phosphite and lactone compounds such as butyrolactone.

Other additive and modifier

Examples of some of the additives/ modifiers could be introduced into epoxy matrix are listed in Table 2.3.

Table 2.3: Additives and modifiers in epoxy system

Additive/ modifier	Function	Example
Filler	Reduce formulation cost, shrinkage, and water absorption. Improve toughness and abrasion resistance,	Aluminium, zirconium silicate. arsenic pentoxide, barium sulphate, beryllium oxide, calcium carbonate, carbon black, copper, colloidal silica, fibrous glass, graphite, kaolin clay, silica, silver, and talc
Plasticiser/ flexibiliser	Alleviate the inherently hard and brittle characteristics of epoxies	Aliphatic polyesters, polyamides, and polysulfides
Toughening agent	Increase resistance to crack propagation	Rubber, carboxyl-terminated poly(butadiene-co-acrylonitrile)s
Resinous modifier	Enhance thermal stability, flame retardant property, adhesiveness, corrosion resistance, and chemical resistance	Nylon-epoxies and polysulfide-epoxies exhibit toughness improvements (Lewis, 1988); phenolics-epoxy own higher temperature capability; halogen in epoxy network assist to lower water absorption

2.2.2 Reaction mechanism and chemistry of epoxides

Epoxides are three-membered ring cyclic ethers which are very susceptible to ring-opening reaction owing to the extreme ring strain. Epoxy functional groups react readily with various chemicals is shown in Figure 2.5.

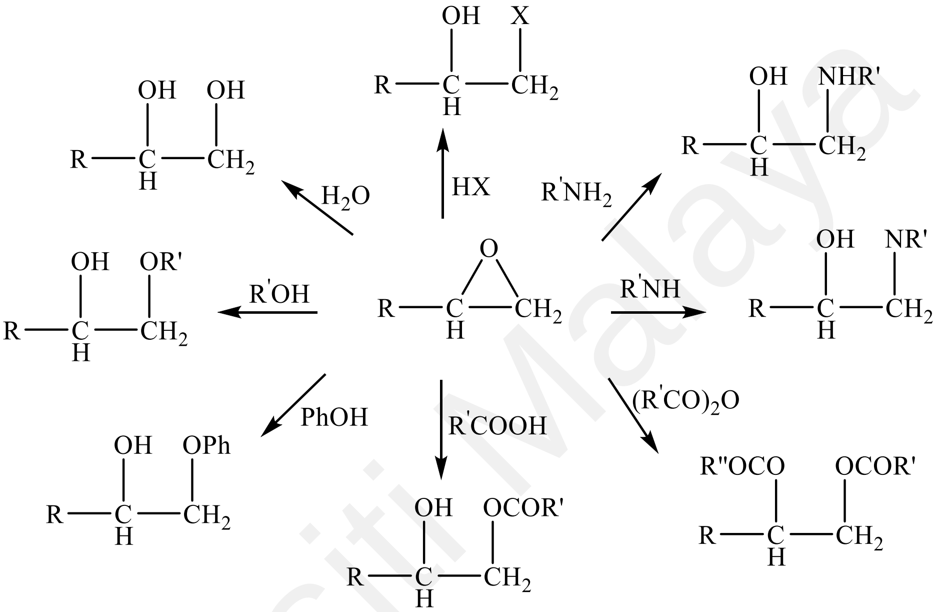


Figure 2.5: Reactions of epoxy functional group

2.2.2.1 Polymerisation of epoxides

Ring-opening polymerisation of epoxides can be occur through cationic and anionic mechanism which includes steps similar to other conventional polymerisation which are initiation, propagation and termination process.

(a) Cationic ring-opening polymerisation of epoxides

In order to initiate the reaction, cationic active centers are generated by reaction of addition of electrophile to the epoxide oxygen atom. Initiators used in cationic epoxy ring-opening polymerisations include protonic acids such as sulphuric acid, triflic acid, and trifluoroacetic acid and Lewis acids used in conjuction with co-catalysts such as $PhC^+[PF_6]^-$ and $CH_3CO^+[SbF_6]^-$. The simplest epoxies, ethylene oxide is used as an example to illustrate the initiation, propagation and termination reaction shown in Figure 2.6. R^+A^- is representing the initiator.

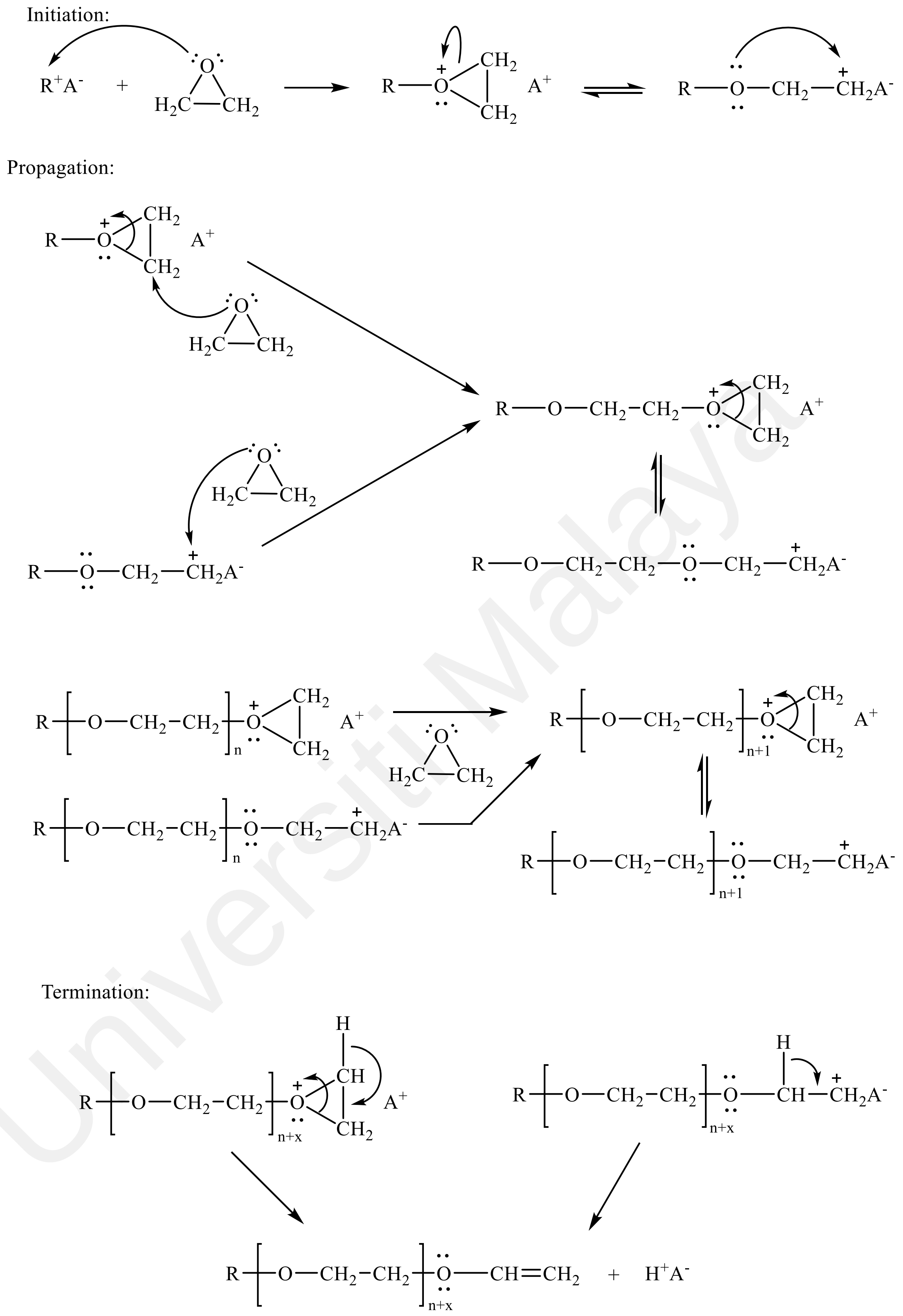


Figure 2.6: Mechanism of cationic ring-opening polymerisation of epoxies

Initiation occurs by addition of R^+ to epoxide oxygen atom to produce a cyclic oxonium ion and corresponding open-chain carbocation. In addition step, one lone pair of epoxide oxygen atom is transferred to R^+ to form bonding, thus result a positive charge oxonium ion. Transferring a pair of electrons from C-O bond to the positively charged epoxide oxygen atom leads to the breaking of oxonium ion ring, and the positive charge is transferred to the carbon hence create a positively charged carbocation. The oxonium ion and carbocation products are in equilibrium as the transferring of electron pair is reversible. Both of them undergo the next propagation step. Oxonium ion is propagated through ring-opening of cyclic oxonium ion caused by the nucleophilic attack of an epoxide oxygen atom in another monomer to the ring carbon atom. For carbocation, addition of monomer happens via transferring of one lone pair epoxide oxygen in another monomer to the positively charged carbon. Similar to the initiation step, the initial product of the propagation step has a terminal cyclic oxonium ion formed from the newly bonded monomer molecule and it is in equilibrium with open-chain carbocation. Termination take places through a rearrangement reaction of the terminal oxonium ion ring and ionic part of compounds. An unsaturated C=C end group is formed through elimination of H^+ (Young & Lovell, 2011).

(b) Anionic ring-opening polymerisation of epoxides

Initiators used in anionic epoxy ring-opening polymerisations include alkali metals, inorganic bases, metal alkoxides, metal alkyls and halides, and electron transfer complexes. The polymerisation using M^+A^- to represent the initiator is shown in Figure 2.7.

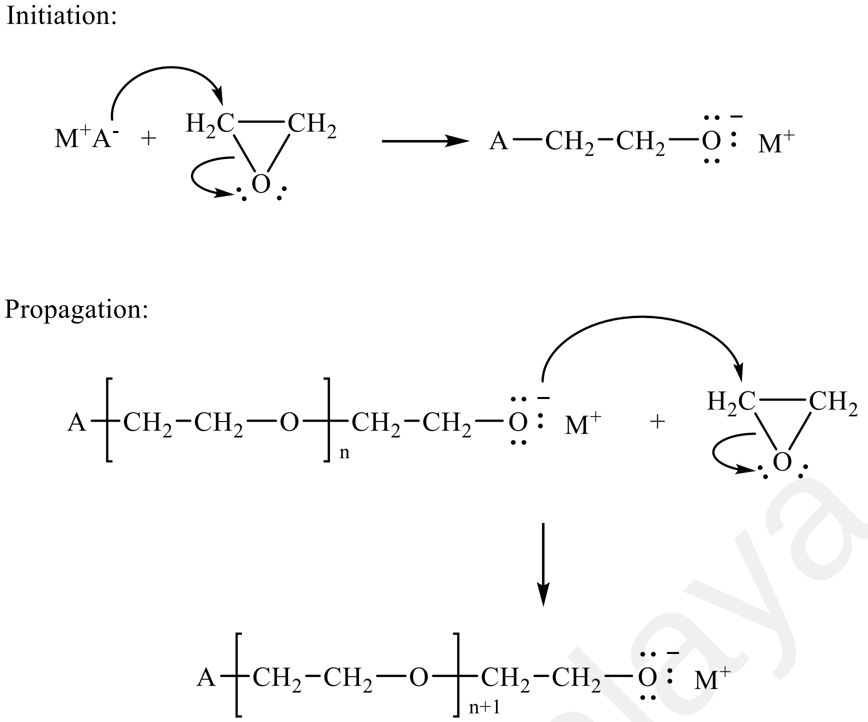


Figure 2.7: Mechanism of anionic ring-opening polymerisation of epoxies

Initiation take places through nucleophilic attack by A^- nucleophile to the oxirane ring. Addition of A^- into epoxide by transferring one lone pair of electrons from A^- to the ring carbon atom, then an electron pair is transferred from C-O bond to epoxide oxygen atom, C-O bond is broken and oxirane ring is opened. Product resulted with a negatively charged oxygen atom and balanced with counter ion M^+. In propagation step, the addition of other monomers occurs through nucleophilic attack by negatively charged epoxies oxygen atom to oxirane ring in another monomer. For substituted epoxides, nucleophilic attack of monomer by active anion take place at the least sterically hindered carbon atom. There is no inherent termination reaction, thus the polymeric anions remain active unless a proton donor is added deliberately to terminate the polymerisation when the degree of conversion is achieved (Young & Lovell, 2011).

2.2.2.2 Curing of epoxides

Curing system of epoxy resins include room-temperature curing in which reactions take place at room temperature; heat curing by reacting at elevated temperature; and photo curing with the presence of infrared, ultraviolet light, or electron beam irradiation. The reactions between epoxide groups of epoxy resins and functional groups of hardener involve either electrophilic attack on the epoxide oxygen atom or nucleophilic attack on one of the ring carbon atoms. Ring opening of epoxy resins by nucleophiles and electrophiles are demonstrated in the previous section. Properties of cured epoxies vary from reactions with different hardeners and various curing processes.

The thiol or mercaptan group (-SH) is able to react with epoxy resins in the presense of co-curing agents or basic catalysts to promote the production of reactive mercaptide ions (Pham & Marks, 1991). Co-curing agents/ co-catalysts such as polyamides, polyamidoamines, cycloaliphatic amines and tertiary-amine accelerate cure meanwhile, in some cases, improve the properties of cured polymers especially the mechanical properties (Ashcroft, 1993). The proposed curing mechanism of epoxy resin with thiol group is shown in Figure 2.8 which is supported by the findings of Kamon et al. Nitrogen atom in tertiary amine transfers a lone pair of electron to the thiol group, create a mercaptide ion which capable to react with epoxy resin. Addition of thiol-containing curing agent take places through nucleophilic attack by active mercaptide ion to oxirane ring of epoxy resin. The resulting negatively charged oxygen atom attracts a hydrogen atom from thiol group forms a neutralised product, a new active mercaptide ion is formed. The addition reaction is continued by repeating the reaction with newly formed mercaptide ion.

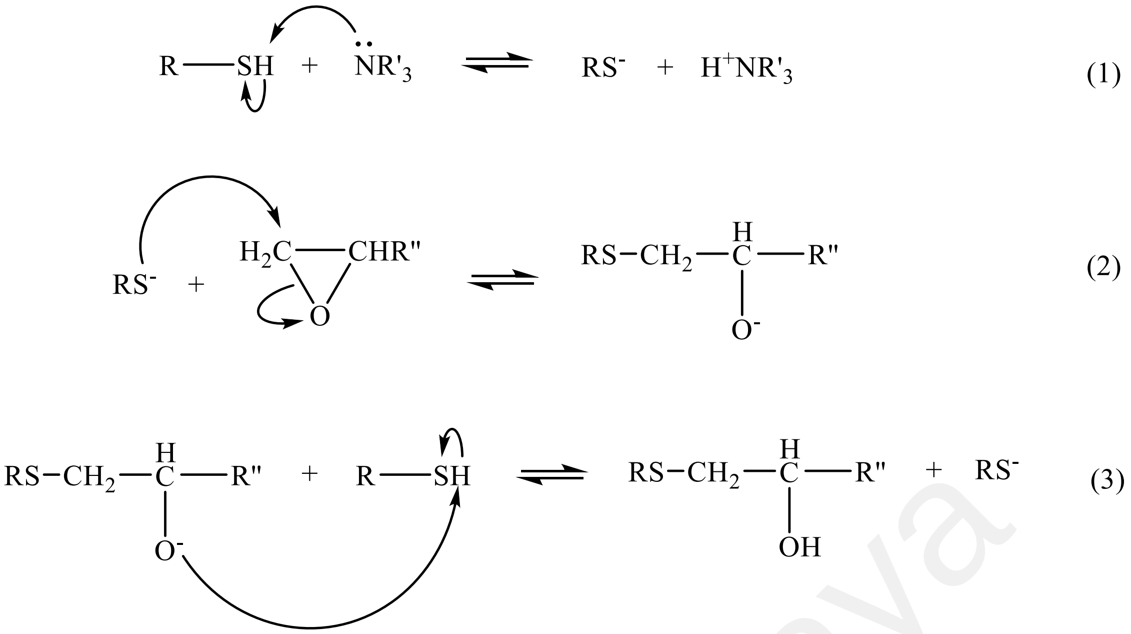
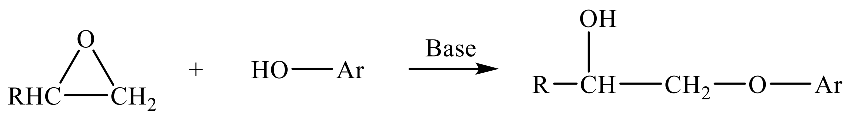
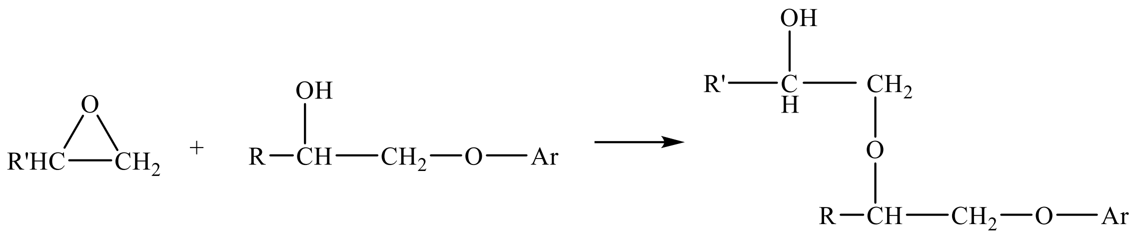


Figure 2.8: Reaction mechanism of epoxy resin with thiol group

Lewis bases are normally used to speed up the reaction between epoxides and phenolic hydroxyls. The reaction take places through the addition of the phenolic hydroxyls to epoxides in the presence of base catalysts. This generates product with secondary hydroxyl groups. The occurrence of secondary hydroxyl groups to react with remaining epoxide groups, so called the second reaction is depended on the nature and concentration of accelerator as well as the reaction temperature. In general, the epoxide-phenol reaction is preferably over the epoxide-secondary hydroxyl reaction under condition of either selective or less selective accelerators (Hale et al., 1989). The reaction between epoxide group and phenolic hydroxyl group is shown in Figure 2.9.



Main reaction



Second reaction

Figure 2.9: Reaction between epoxide group and phenolic hydroxyl group

2.2.3 Petroleum-based epoxy coatings

Due to the easy processing of epoxy resins as well as superior in heat resistance, adhesion property, corrosion resistance, and mechanical property among thermosetting resins, they are widely applied in coatings, adhesives, industrial tooling, aerospace industry, electronic materials, and biomedical systems. Other than miscellaneous excellent properties, quick curing and low shrinkage upon cure account to the popularity of epoxy coatings.

Safaei et al. synthesised an epoxy coating modified with epoxy-microcapsule which has potential applications in industrial coating and paint systems. 10 wt% of microcapsule which cored with the healing agent, a low viscosity epoxy resin, EPL 1012 was mixed into the diluted EPON 828 epoxy resins at ambient temperature. Modified polyaminoamide adduct, Merginamide A280 was added into microcapsule-containing epoxy system to act as hardener. The epoxy formulation was cured at room temperature for 7 days. The cured epoxy coatings exhibited astonishing corrosion resistance and excellent self-healing property (Safaei et al., 2018).

Ai and companions synthesised waterborne epoxy coatings from two type of bisphenol A-based epoxy resins and one phenol novolac epoxy resin respectively. Waterborne epoxy dispersions were first produced from the epoxy resins and as-prepared emulsifier, followed by mixing the waterborne epoxy dispersions with waterborne curing agent correspondingly. The films were cured at room temperature for 7 days. The cured coatings exhibited excellent wear resistance, thermal stability, and mechanical properties (Ai et al., 2019).

Kowalczyk et al. produced a series of waterborne and solvent-based epoxy coatings based on bisphenol-A based epoxy resins with varying types and ratios of nanofillers, modified montmorillonites. The modified montmorillonites were dispersed in epoxy resins, followed by curing with different types of amine hardeners at room temperature for 14 days. All formulation of coatings with modified montmorillonites shown improved scratch resistance, abrasion resistance and water resistance compared to coatings without modified montmorillonites. There were enhancements with respect to other properties shown in some of the coating formulations, depending on the amount and type of nanofiller added (Kowalczyk & Spychaj, 2008).

Atta et al. reported the synthesis of novolac epoxy resins derived from bisphenol A for coating applications. Bisphenol A novolacs were prepared by two different routes from reacting bisphenol A with *p*-formaldehyde and formalin solution respectively. Epichlorohydrin was used to react with bisphenol A novolacs in the production of diglycidyl ether bisphenol A novolac. Novolac epoxy resins were cured with 1-(2-amino ethyl) piprazine hardener to form epoxy coatings. The cured coatings showed good chemical resistances and mechanical properties (Atta et al., 2008).

UV-curable epoxy coatings were produced by Bajpai and companions from acrylated phenol and cresol novolac resins. Condensation between phenol/ cresol and formaldehyde yielded novolac resins, which then was reacted with epichlorohydrin to form novolac epoxy resins. After that, they was acrylated by using acrylic acid. The mixtures of acrylated novolac resins, reactive diluents, organosilicon compound and photo-initiator were cured under UV irradiation. The coatings exhibited improved thermal stability, chemical resistance and corrosion resistance by incorporating of silicon compounds (Bajpai et al., 2005).

Shen et al. synthesised a series of UV-curable oligomers for temporary protective coatings based on bisphenol F epoxy resin. Modified acrylated epoxy resins were resulting from reaction between bisphenol F epoxy resin, acrylic acid and 2-acrylamide-2-methylpropanesulfonic acid (AMPS). The prepared resins with different ratios of acrylic acid and AMPS were UV-cured at room temperature after mixing with photoinitator. Cured modified epoxy coatings showed enhancement in elongation at break and adhesive strength after introduction of AMPS. The hydrophilicity of coatings was also increased by the incorporation of sulfonate and amide groups (Shen et al., 2015).

2.2.4 Bio-based epoxy coatings

There are raising attention on developing the bio-based epoxy resins, this is driven in part by considering the depletion of fossil fuels, and in part by the worsen environmental issue such as global warming. Majority worldwide epoxy resin materials are made up from petroleum derivative such as bisphenol A, bisphenol B, bisphenol F and novolac. Other than impact on environment, the key precursor, bisphenol A has found to cause deleterious effect to human health due to its toxicity and ability to act as endocrine disruptor, same to its analogues bisphenol B and bisphenol F (Usman et al., 2019). In aspect of health and safety, their usage in epoxy coatings are concerned especially internal coatings of food and beverage cans. Keeping in view of the commercial importance of epoxy coatings as well as the critical sustainable development, there are copious studies focus on formulating green epoxy coatings by (i) utilising bio-based epoxy resins, and (ii) implementing natural-resourced modifiers and/or hardeners to impart the eco-friendliness on coatings (Kumar et al., 2018; Baroncini et al., 2016; Yan et al., 2018).

Kugler and companions have successfully produced epoxy powder coatings from natural-based epoxy resins, hardeners and fillers. A tri-functional bio-based epoxy resin was synthesised from reaction between 75% abietic acid-containing rosin with epichlorohydrin. Two types of anhydride curing agents were produced from a two-step process by first reacting rosin with diols, followed by reaction with maleic anhydride. Anti-corrosive fillers were prepared from natural halloysite. Coatings were formed by thermal curing the fine powders of resins, hardeners and fillers at elevated temperature after the process in knife mill. This eco-friendly coatings exhibited satisfying and comparable/slightly improved performance with the reference petroleum-based coating. Based on the properties shown by coatings, the naturally-derived compositions had potential for replacement of commercial petroleum-based epoxy binders in powder coating formulation (Kugler et al., 2021).

Kanehashi et al. synthesised a series of bio-based epoxy resins from cashew nut shell liquid for coating application. Cardanol-based epoxy resins were produced first from epoxidation reaction between isolated cardanol from cashew nut shell liquid and epichlorohydrin, followed by thermal polymerisation under different temperature, time and atmosphere. Epoxy coatings were prepared by reacting cardanol epoxy resins with different types of amine curing agents at room temperature. Cured coatings showed good chemical resistance, satisfactory thermal stability and curing time (Kanehashi et al., 2013).

Vegetable oil is one of the natural resources utilised widely in producing bio-based epoxy resin. Renewable environmentally friendly epoxy resins for surface coatings were produced by Shaker and companions. Modified oil-based epoxy resins were synthesised first by epoxidising sunflower, soybean and linseed oils using peroxy acetic acid as the epoxidized agent, followed by reaction with N-(2-hydroxyethyl) phthalimide. Phthalimide-epoxy resins were air dried for 10days then cured at elevated temperature to form epoxy films. Cured epoxy films exhibited good water, alkaline and solvent resistances (Shaker et al., 2008).

Zheng et al. synthesised hydrophobic bio-based epoxy coatings for anti-corrosion application. A dispersion solution were prepared by mixing the hydrophobic curing agent Dynasylan F8815, superhydrophobic SiO_2 nanoparticles and hydrophobic modifier hexadecyltrimethoxysilane using deionised water as the solvent. After the isosorbide based epoxy resin solution was prepared by mixing isosorbide based epoxy resin with deionised water, it was mixed with the as-prepared curing agent solution under vigorous stirring. The resin mixture was cured at elevated temperature to form coatings. This green epoxy coatings possessed high hydrophobicity, high water repellence, good mechanical robustness against sands erosion, and corrosion resistance (Zheng et al., 2019).

Patil et al. manufactured a phosphorus-containing epoxy resin from sebacic acid for flame-retardant coating application. Sebacic acid is a naturally occurring dicarboxylic acid which its usage in resin synthesis for coating applications is reported. A phosphorus-containing reactive diol was obtained from reaction between N-methylethanol amine, N-methylethanol amine and phenylphosphonic dichloride. Sebacic acid was then reacted with it to form phosphorus-containing dicarboxylic acid. The flame-retardant epoxy resin was produced by reacting sebacic acid with epichlorohydrin. Naturally-resourced epoxy resin was mixed with petroleum-based epoxy resin in different ratio, and then thermal cured with polyamide hardener to form coatings. Coatings with added sebacic acid-based epoxy resin exhibited good mechanical properties, chemical and solvent resistance similar to the conventional coatings. The char yield increased and the flame-retardant properties of coatings improved with the concentration of the sebacic acid-based epoxy resin. Sebacic acid-based epoxy resin was evidenced as a good partial replacement for conventional bisphenol A-based epoxy resin for flame-retardant coating formulation (Patil et al., 2019).

Modified epoxy novolac resin derived from renewable resource was synthesised by Yadav et al. for surface coating application. Epoxidized novolac resin was prepared from the epoxidation of cardanol-based phenol novolac resin with epichlorohydrin. Cardanol-based novolac resin was manufacture by reaction between cardanol and formadehyde. Modification on resins was carried out by blending cardanol-based epoxidized novolac resins with various concentrations of carboxyl-terminated poly(butadiene-co-acrylonitrile), a liquid rubber. Rubber modified novolac resins were thermal cured with polyamine curing agent. Modified films exhibited improved solvent resistance, gloss, scratch hardness, adhesion, and flexibility compared to that formulated from pure epoxy resin (Yadav et al., 2009).

The bio-based epoxy coatings prepared in last few decades show comparable performance and properties as the petroleum-based epoxy coatings in aspect of corrosion resistance, thermal stability, chemical resistance and mechanical strength. Thus, the bio-based materials could be an alternative choice to form coatings with potential replacement for conventional petroleum-based coatings.

2.3 Alkyd coatings

2.3.1 Background

Alkyd resins produced from polyhydric alcohols, polybasic acids, and monobasic fatty acids (saturated or unsaturated) have been utilised in coating industry since long time ago. Alkyd resins have been named in many other ways includes “alkyd”, “polyester”, “glyptal” and “glycerolphthalic”. The term “alkyd” that is most commonly used now was created in 1914 by Kienle, which refer to the combine of words “alchohol” and “acid”, indicating the polycondensate made up from fatty acids, polyols and polyacids. The first alkyd resins were attempted by Berzelius in 1847 by reaction of tartaric acid and glycerol. In year 1853, Berthelot prepared the glycerol ester resin by using camphoric acid. Subsequently, other chemists began to prepare resins from the reaction between glycerol with other polyacids including succinic acid, citric acid, and mixture of succinic and benzoic acids. Smith synthesised glycerol phthalate resin from glycerol and phthalic anhydride in year 1901. The term “glycerophthalic” appears since the first resins produced based on glycerol and phthalic anhydride. Kienle modified glycerol phthalic-based resins by introducing natural fatty acids, which then formed into protective coatings after cured by air drying or low temperature heating. The formed resins were commercialised by General Electric under trade name “Glyptal”. Chemists from Bayer laboratories discovered the transesterification process of oils in 1927, which was a great development to enable the direct use of oils as basic components and serve as alternatives for fatty acids in alkyd formulation (Deligny & Tuck, 2000). The progression of alkyd resin technology was continued by varying the use of different polyacids, polyols, oils and fatty acids which were new to be introduced into the formulation. Other than the choice of raw materials, modification of alkyd resins with other resins or reactants, as well as the the sequence of introducing the reacting materials during the cook could alter the properties of alkyd resin produced, leading to innovation of alkyd coatings with various characteristics.

2.3.1.1 Raw materials

(a) Oil and fatty acid

Oil or fatty acids are introduced into alkyd system by adding whole oil or fatty acids directly. Oil contain of mixture of simple triglycerides and mixed triglyceride. Simple triglycerides are made up from three identical fatty acids while mixed triglycerides compose of different fatty acids. Fatty acids can be categorised into saturated and unsaturated fatty acids, with the latter referring to those with C=C. Examples of fatty acids and their compositions are shown in Table 2.4.

Table 2.4: Examples of fatty acids

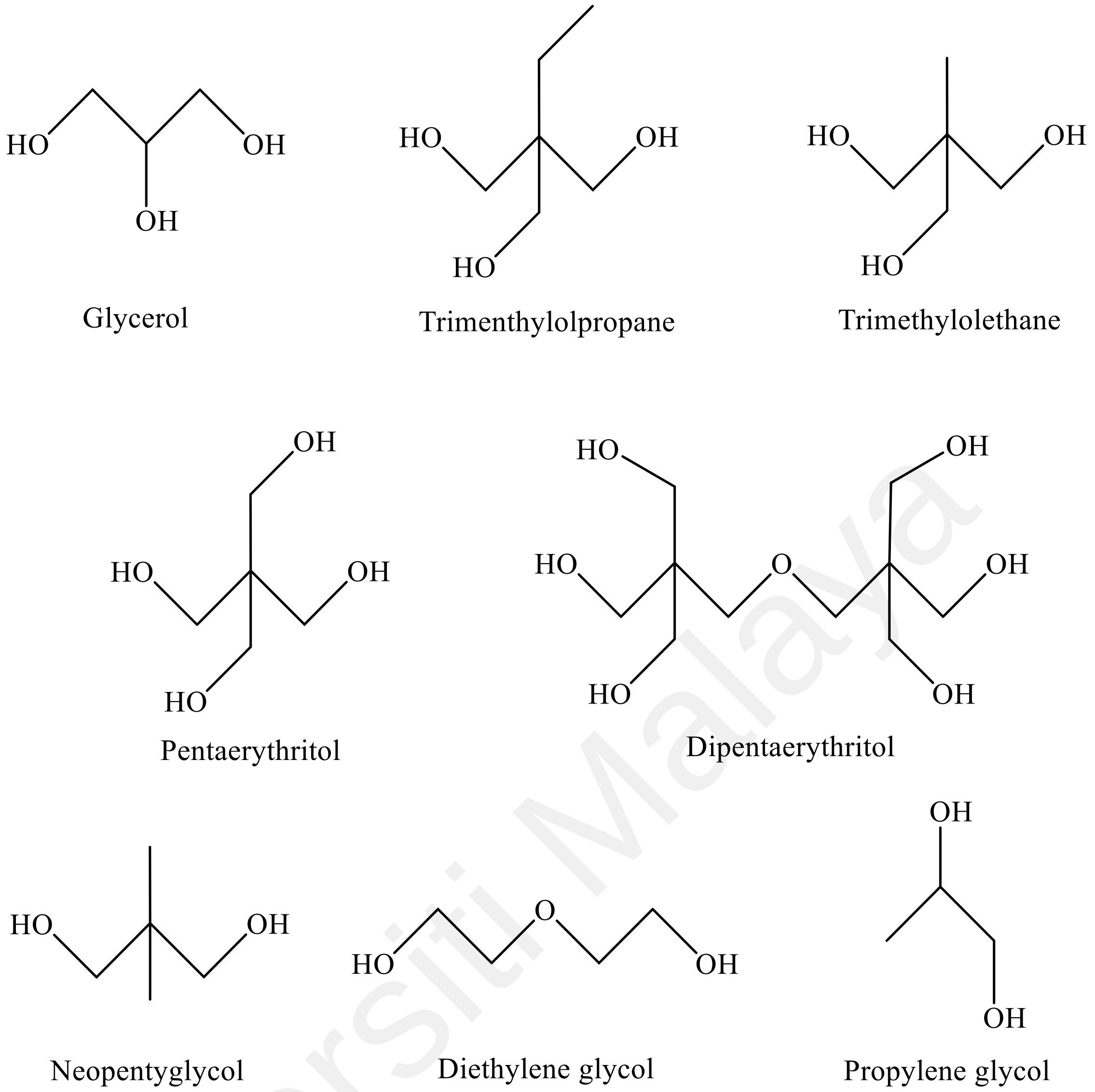
Fatty acid	Structure (carbon:double bond)	Type	Formula
Lauric	12:0	Saturated	$C_{12}H_{24}O_2$
Myristic	14:0	Saturated	$C_{14}H_{28}O_2$
Palmitic	16:0	Saturated	$C_{16}H_{32}O_2$
Stearic	18:0	Saturated	$C_{18}H_{36}O_2$
Arachidic	20:0	Saturated	$C_{20}H_{40}O_2$
Behenic	22:0	Saturated	$C_{22}H_{44}O_2$
Lignoceric	24:0	Saturated	$C_{24}H_{48}O_2$
Oleic	18:1	Unsaturated	$C_{18}H_{34}O_2$
Ricinoleic	18:1	Unsaturated	$C_{18}H_{34}O_3$
Linoleic	18:2	Unsaturated	$C_{18}H_{32}O_2$
Linolenic	18:3	Unsaturated	$C_{18}H_{30}O_2$
Oleostearic	18:3	Unsaturated	$C_{18}H_{30}O_2$
Erucic	22:1	Unsaturated	$C_{22}H_{42}O_2$

Types of oil used in the alkyd synthesis affects drying ability of alkyd resins primarily due to the difference in the degree of unsaturation present in the oil. Oil can be divided into three types; drying, semi-drying and non-drying oil depending on the types and amounts of unsaturation present in their fatty acid components. Drying oil has high percentage of unsaturation with iodine values of over 150, semi-drying oil has lower percentage of unsaturation with iodine values the range of 100-150. Non-drying oil has low unsaturation and low iodine values which are less than 100. The iodine values for classifications may vary slightly in different literatures. Aside from the quantity, the types of unsaturation also influences the drying rates of oils. Oil that contains substantial amount of conjugated double bonds have faster drying rates than the isolated one as the conjugation could accelerate the oxidative drying process. Alkyd resins prepared from oils with high iodine values tend to have shorter drying time. Examples of drying oils are linseed oil, tung oil and perilla oil; semi-drying oils are soybean oil, safflower oil, sunflower oil and rubber seed oil; whereas non-drying oils include castor oil, cottonseed oils, rapeseed oil and coconut oil (Karak, 2012). Selection of oil may also affect the colour of the alkyd resins produced. Drying oils generally cause more obvious yellowing compared to semi-drying and non-drying oils.

The proportions of oil added into an alkyd formulation could affect the properties of alkyd produced. Alkyds are classified into three groups which are short oil alkyds, medium oil alkyds, and long oil alkyds based on the relative amount of oil in the formulation. Short oil alkyds usually contain <45% oil, medium oil alkyds comprise of 45–55% oil while long oil alkyds are cooked with >55% oil (Oldring, 2003). Short oil alkyds possess high viscosity, good substrate adhesion, water resistance and hardness but they have limited compatibility with many aliphatic solvents. They are generally applied as anti-corrosive primers, car refinishes and road paints. Long oil alkyds exhibit outstanding gloss and wetting of pigments but suffer from poor hardness, alkaline sensitive and poor exterior resistance. They are mostly used in building interiors, gloss finishes, wood varnishes and marine application such as primers (Deligny & Tuck, 2000).

(b) Polyhydric alcohol

There are diverse chemical compounds used as polyhydric alcohols, also called polyols in the synthesis of alkyd resins. Several examples of polyols which are commonly used is shown in Figure 2.10. Glycerol is the first polyol to be utilised in preparation of alkyd resins, and it is a triol. It is a valuable renewable component in the synthesis of alkyd resins and is easily available (Oldring, 2003). Another example of polyols is trimethylolpropane, TMP which contains three hydroxyl groups and all of them are primary hydroxyls which are equally reactive. Other than relatively lower viscosity exhibited by alkyd resins made with TMP, properties such as exterior durability, water and alkaline resistance are also enhanced. Trimethylolethane, TME has similar properties with TMP but provide slight improvement in heat resistance of alkyd resin. Example of polyols with functionality of 5 includes pentaerythritol, and it is typically used in long oil alkyd resins. Alkyd resins prepared from pentaerythritol dry faster than trihydric alcohols, and they show outstanding adhesive property, better water and chemical resistance, and longer lasting colour and lustre in comparison with triols. Hexafunctional alcohol such as dipentaerythritol enable the formation of long oil alkyd resin up to 90% and often used in high solid alkyds. Other than multi-functional alcohols, diols have been used in alkyd resin formulation, such as neopentylglyvol, diethylene glycol and propylene glycol. Some glycols provide high flexibility and low hardness to alkyd resins (Deligny & Tuck, 2000).



Glycerol Trimenthylolpropane Trimethylolethane

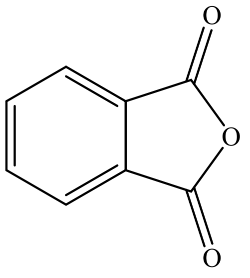
Pentaerythritol Dipentaerythritol

Neopentyglycol Diethylene glycol Propylene glycol

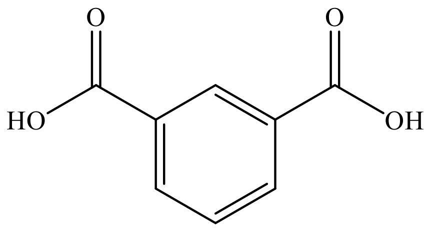
Figure 2.10: Polyhydric alcohol commonly used in alkyd resin synthesis

(C) Polybasic acid

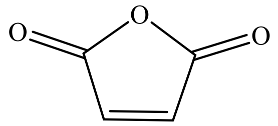
Polybasic acids, also known as polyacids in forms of aliphatic, aromatic or anhydride derivatives are utilised in the synthesis of alkyd resins. Several examples of polyacids which have been used in alkyd synthesis are shown in Figure 2.11. Phthalic anhydride, PA is one of the most widely used diacids in alkyd resin synthesis. Phenyl groups in the main chain of PA-derived alkyd could resist the main chain rotation, and consequently improve the hardness and chemical resistance. Another excellent candidate choice of polyacids is isophthalic acid. It incurs higher molecular weight in alkyd resins compared to phthalic acid owing to its greater tendency for cyclisation with polyols. It improves the drying rate, resistances to corrosion, yellowing and hydrolysis as well as hardness. Maleic anhydride also offer prominent enhancement in drying properties and hardness of alkyd resins. Trimellitic anhydride is generally used in water soluble alkyds as well as high solid alkyds (Deligny & Tuck, 2000). Other than rigid aromatic rings, cycloaliphatic rings in hexahydrophthalic anhydride can also increase T_g of the alkyd (Wicks et al., 2007). Aliphatic diacids such as adipic acid and azelaic acid are commonly used to plasticise alkyd resins to afford flexibility, shock and impact resistance due to its linear structure. Dimer acids formed from dimerisation of fatty acids can significantly increase the flexibility of the alkyd resins.



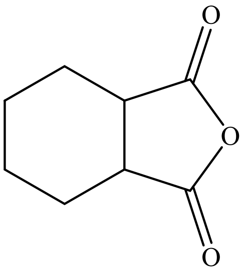
Phthalic anhydride



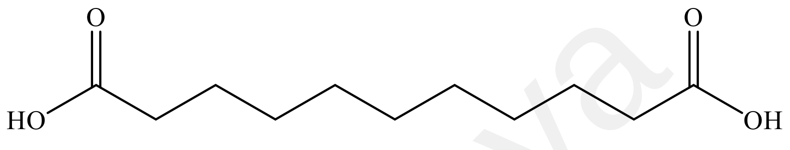
Isophthalic acid



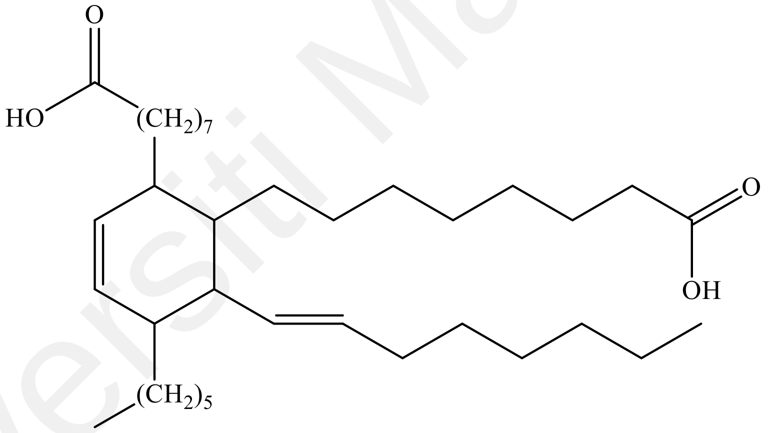
Maleic anhydride



Hexahydrophthalic anhydride



Azelaic acid



Dimer acid

Figure 2.11: Polybasic acids commonly used in alkyd resin synthesis

2.3.1.2 Catalyst

In alkyd synthesis, catalyst is added to carry out reaction at lower temperature, specifically during the alcoholysis step to convert glycerol or polyol into monoglyceride. Although this can be achieved without catalyst, higher temperature is usually necessary. With presence of suitable catalyst, the temperature can be cut down from 288 ˚C to 232-249 ˚C. Besides, rate of conversion can also be accelerated and the loss of volatiles can be reduced significantly. However, as little catalyst as possible should be added into alkyd system because it promotes colour development. Calcium hydroxide and lead oxide are common catalysts used for alcoholysis at 0.05 to 0.1% of the oil weight. Other examples of catalysts include barium oxide, barium hydroxide, barium naphthenate, calcium oxide, calcium naphthenate, lead napthenate, lithium hydroxide, lithium naphthenate, lithium ricinoleate, sodium hydroxide, sodium naphthenate, sodium naphthenate, and zinc oxide.

2.3.1.3 Modifier

Alkyd resins can be physically and chemically modified to improve some specific properties such as drying, application and protective strength (Deligny & Tuck, 2000). Examples of modifiers that have been used in alkyd modification are summarised in Table 2.5.

Table 2.5: Modification of alkyd

Modifier	Details of modification	Resultant properties	Applications
Styrene	Copolymerisation using styrene in alkyd synthesis	Pros: Improved drying rate, enhanced hardness, water and alkaline resistances, and good adhesion on metals. Cons: Poor solvent resistance	Quick air-drying industrial paints, metal finishes, and anti-corrosive primers
Vinyl toluene	Copolymerisation using vinyl toluene in alkyd synthesis	Pros: Shorter drying time, improved hardness, enhanced water and alkaline resistance Cons: Poor solvent resistance	Coatings applied on knifes, anti-corrosive primers and fast drying industrial paints.
Epoxy	Epoxy act as polyol in alkyd synthesis	Pros: Excellent adhesion to metal, outstanding corrosion resistance, and improved chemical resistance Cons: Risk of loss of gloss	Anti-corrosion paints, coat finishes for heavy goods vehicles and can coatings.
Nitrocellulose	Nitrocellulose physically blended with alkyd	Pros: Quick drying and high gloss properties Cons: Limited resistance to temperature and solvents	Automobile and cycle industries
Urea formaldehyde	Urea formaldehyde physically blended with alkyd	Pros: Flexibility, water impermeable, acid and alkaline resistance, good hardness, and stable towards light and heat Cons: Limited solvent resistance	Stoving system in industry application and car industry

2.3.2 Alkyd synthesis

(a) Monoglyceride and fatty acid procedure

When whole oil is used for alkyd synthesis, monoglyceride procedure is carried out. Fatty acid procedure on the other hand involves direct introduction of selected fatty acids into the system. The pros and cons of using whole oils and fatty acids are summarised in Table 2.6. By and large, whole oil is chosen as raw material when pricing take primacy especially in producing long oil alkyds, whereas, fatty acid is preferred when performance takes the priority, since it gives greater latitude in alkyd design to achieve certain specific properties.

Table 2.6: Advantages of using fatty acids or vegetable oils in alkyd synthesis

Fatty acids	Vegetable oils
(a) Any polyol or polyol blend can be used in alkyd cooking.	(a) More economical.
(b) Selection of fatty acid to meet specific performance is possible.	(b) Discolouration is less likely to happen during storage
(c) Order of addition of fatty acid can be controlled to attain different alkyd characteristics.	(c) Oil is less corrosive, corrosive resistance equipment is not necessary.

(i) Monoglyceride process

This process involves two steps; alcoholysis followed by polyesterification. Alcoholysis reaction converts triglyceride and polyol into homogenous predominant monoglyceride phase. Then, the monoglyceride serve as solvent for polyacid added in next step, and polycondensation between monoglyceride and polyacid take place at higher temperature to produce alkyd resins. The level of completion of transterification reaction is usually monitored by checking the solubility of alcoholysis product in methanol or ethanol. The starting oil is insoluble in alcohol, while the product dissolves well in it. Figure 2.12 show an alcoholysis reaction using glycerol as an example. The characteristics of alkyd produced from monoglyceride procedure includes softer, tackier, and better resistance towards hydrocarbon solvents.

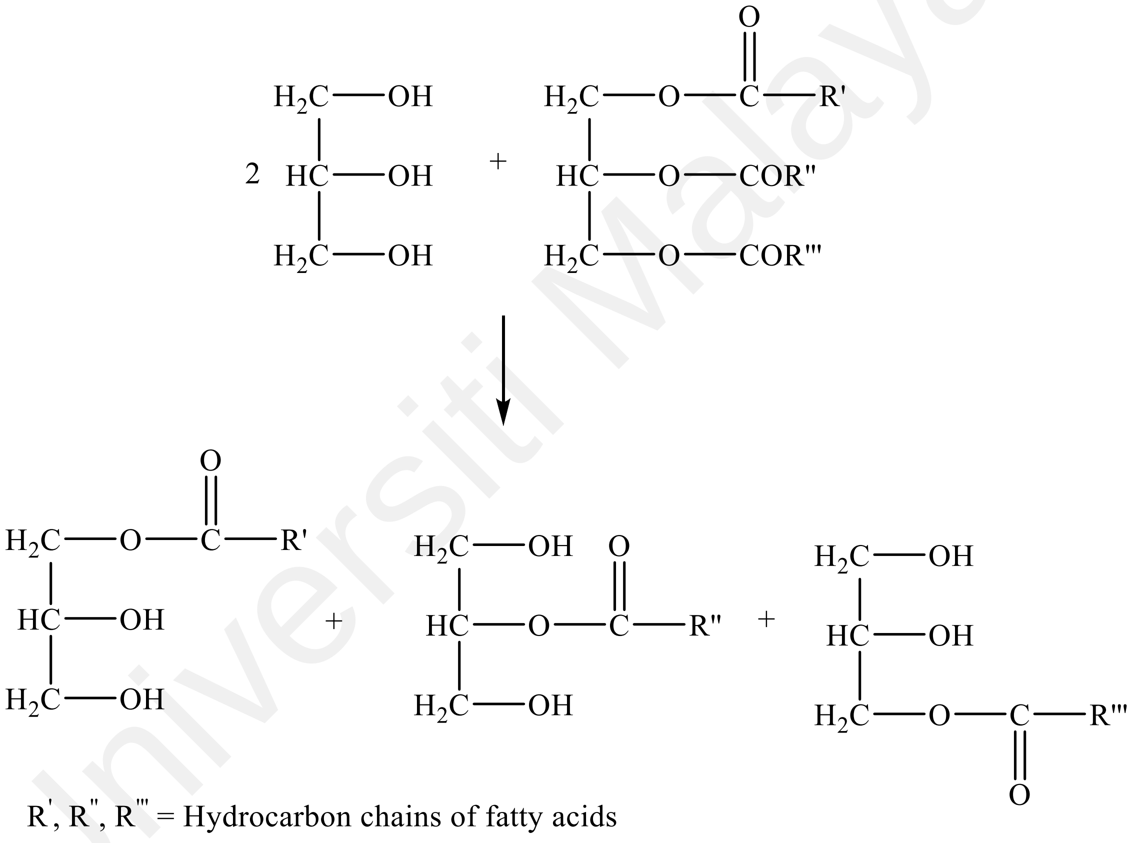
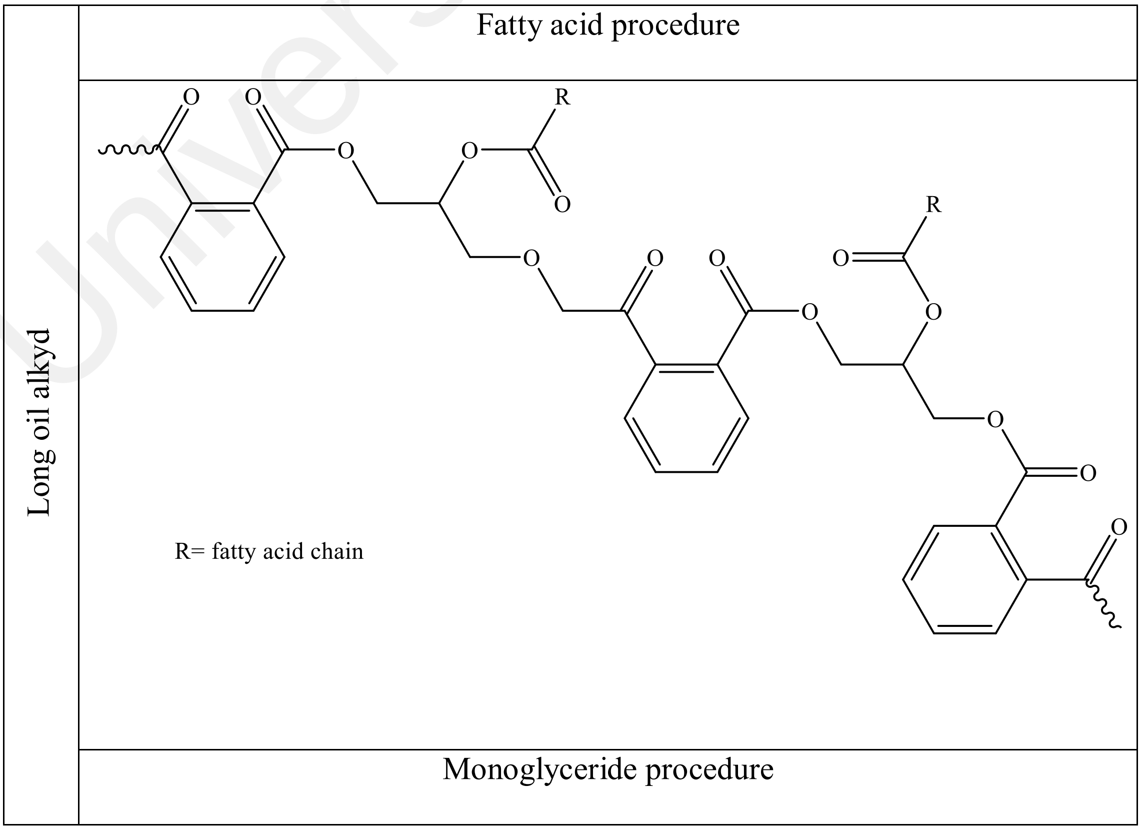
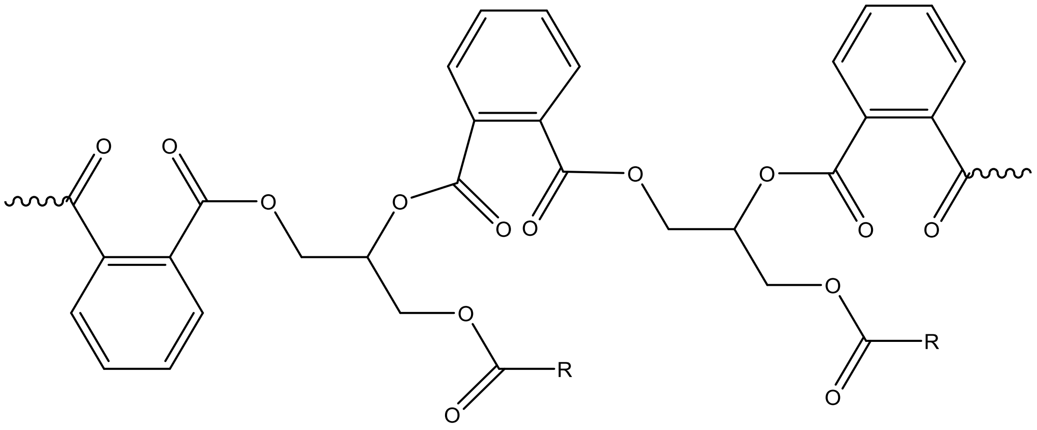


Figure 2.12: Transesterification reaction involving triglyceride and glycerol

(ii) Fatty acid process

In typical fatty acid process, all reactants are added into reaction flask from the start, and all the fatty acids and polybasic acids directly compete to react with the polyols. The order of addition of raw materials can however be manipulated to build up the desired structures. The properties of alkyd resins vary for predominantly linear or high molecular weight polymer structures. High polymer alkyd is achieved by "high polymer technique" which introduces a proportion of total fatty acid (40 to 90%) at the beginning. The reaction starts by reacting polyols and polyacids to desired condensation level, the remaining fatty acid is added to esterify with polyols. High polymer alkyds exhibit higher viscosity, improved drying, hardness, adhesion, and alkaline resistance (Deligny & Tuck, 2000). Proposed chemical structures for alkyd resins formed by the monoglyceride and fatty acid procedures are shown in Figure 2.13. Phthalic anhydride and glycerol are used as examples of polyacid and polyol respectively.





R= fatty acid chain

Figure 2.13: Proposed structures of alkyd resins obtained through monoglyceride and fatty acid procedure

(b) Fusion and solvent cook during polyesterification step

Polycondensation reaction between polyacids and polyols can be carried out in the absence of solvent (fusion cook) or in the presence of solvent (solvent cook). The volume of solvent used in solvent cook is controlled at a relatively low percentage which is about 5 to 10% based on the total alkyd weight. Solvents with high boiling points are preferable, which is at least 24 to 38 ˚C less than the polycondensation temperature such as xylene. Water generated as by product is collected through the Dean-Stark receiver together with the solvent. Solvent should be immiscible with water, so that water can be separated out for measurement and drained off while solvent is normally introduced into system [1]. Solvent cook offers several advantages including (i) easier elimination of water, (ii) better monitoring of cooking temperature and viscosity, (iii) lower risk of gelation during cook, and (iv) cleaner reaction set-up after synthesis. Advantage of fusion cook is the resultant alkyd is relatively pure and does not need to undergo pre-treatment to remove any trapped solvent prior characterizations. It is also easier to achieve the intended polymerisation temperature is easier to achieve without the restraint caused by high amount of solvent.

2.3.3 Alkyd coating

Alkyd resins have been widely used as coatings in various fields due to its excellent film forming ability, easily pigment, and ability to blend with additives to form coatings with different properties for various functions. Properties of alkyds could be varied via selection of raw materials, type of oil or fatty acids introduced, as well as sequence of addition of ingredients.

A study was carried out by Aydin et al. to investigate the effect varying types of anhydrides and oil/glycerol ratios in alkyd synthesis. Alkyds formulated with maleic anhydride (MA) had the highest viscosity due to the presence of double bonds that may undergo crosslinking while phthalic anhydride-based alkyds showed higher viscosity than glutaric and succinic anhydride based alkyds due to the presence of rigid aromatic ring to resist the motion of alkyds. Drying time and physicochemical properties are also affected by the amount and type of reactants used. Other notable improvement in MA-based alkyd includes shortest drying time, best water resistance, and good hardness. Viscosity of the alkyds was also found to increase with lower oil/glycerol ratio. It was also reported that removing excess glycerol after the alcoholysis step could produce alkyd with better water resistance (S. Aydin et al., 2004).

Chiplunkar and companions investigated the effect of different ratio of diacid portions on film properties. Alkyd coatings with higher ratio of phthalic anhydride/ maleic anhydride showed better glossy appearance and higher grade of hardness due to the rigid aromatic moiety presence in PA. Whereas coatings with increased portion of MA have shorter drying time due to the degree of unsaturation increased (Chiplunkar &

Pratap, 2016). Alkyd coatings could undergo various modification process to achieve certain desired properties. Chlorinated rubber seed oil alkyds possess better drying ability than non-chlorinated alkyds (Ikhuoria et al., 2007). The greater the chlorination degree, the shorter the resin drying time. The chlorinated alkyds had been improved in the respect of flame-retardant property.

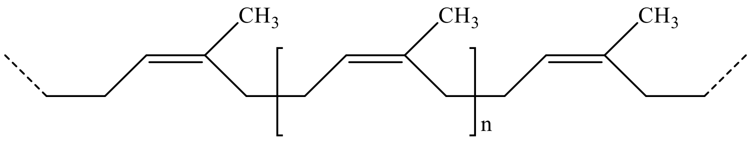
Ang and companions reported the innovation of UV-cured alkyd coatings from palm stearin-based alkyd resins (Ang & Gan, 2012) and in later work they demonstrated the feasibility of utilising epoxidized natural rubbers as crosslinking agents to enhanced property of alkyd coatings (Ang et al., 2013).

For alkyd coating and epoxy coating focused in this work, they exhibit different characteristics and both of them have their pros and cons. Alkyd coating is single pack system while epoxy coating made up from two-component system. Alkyd is relatively low cost, easy to apply, easy pigmented, high gloss, as well as able to blend well with variety of additives. However it takes long time to be fully cured depends on the oil length used. Due to the presence of oil, alkyd coating has limited chemical resistance, it is not suitable to be used in highly chemical environments (especially alkali medium) including applications over galvanizing, concrete, mortar, and most cementitious surfaces. Epoxy coating is hard and durable, possesses good chemical resistance, heat resistance, chemical resistance and adhesion strength. It is widely used in corrosive environment and functioned as protective coating especially for concrete flooring. However, it is difficult to be used in substrate with chronic moisture issues as the epoxy coating may lift off from the surface. In contrast, alkyd coating has excellent ability to adhere to relatively poorly prepared, rough, dirty or chalked surfaces.

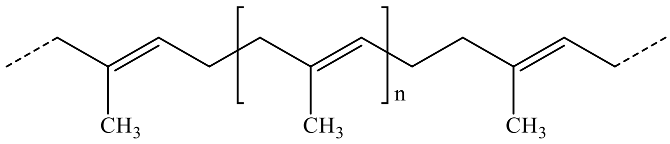
2.4 Natural rubber

2.4.1 Background and history

Natural rubber *cis*-1,4-polyisoprene, is a biopolymer consisting of isoprene units (C_5H_8) linked together in a 1,4 cis-configuration (Hayashi, 2009). Natural rubber is produced from latex, a natural-occurring milky exudate of plant. Approximately 2000 species of higher plants in tropical and temperate regions produce latex from which natural rubber or closely related compounds can be found. Latex from the Para tree, *Hevea brasiliensis* is presently the sole commercial source of natural rubber. Other than the hydrocarbon major component, rubber contains small quantities of protein, carbohydrate, fatty acid, resin-like substance, and mineral salt. These non-rubber components in natural rubber vary from latex depends on its plants origin. Natural rubber, *cis*-1,4-polyisoprene composition obtained by majority rubber-producing plants forms an irregular conformation in the solid state, which is unable to crystallise under normal condition and occurs as an amorphous, rubbery material. The stereoregularity of 1,4-polyisoprene is depend on its source. The isomer *trans*-1,4-polyisoprene are produced by only a few types of plants such as *Mimusops balata,* and *Palaquium gutta* have more regular structures than *cis*-1,4-polyisoprenes. They are able to crystallise and appear as hard rigid material under normal condition (Nor & Ebdon, 1998). The structures of *cis*-1,4-polyisoprene and *trans*-1,4-polyisoprene are shown in Figure 2.14.



cis-1,4-polyisoprene



trans-1,4-polyisoprene

Figure 2.14: Structure of *cis*-1,4-polyisoprene and *trans*-1,4-polyisoprene

Natural rubber is an indigenous of South America, especially the Amazon Valley. Rubber was first used by natives to made waterproof footwear and raincoats with the latex of the Hevea tree by drying them over smoky fires. Christopher Columbus is considered the first European who discover the natural rubber during his second voyage in year of 1493. He realised the natives in Haiti playing with balls fabricated from the exudate of a tree called "cau-uchu" or "weeping wood". The name “rubber” was given by John Priestly in 1770, when he found that the material could “rub off” pencil marks. Rubber was introduced to the Western world by Charles de la Condamine in 1736. Europe and America used a few tons of rubber per year by the end of 18th century. Consumers found it difficult to work with solid rubber and the objects produced from natural rubber turned sticky in hot climate and hardened in the cold. Charles Goodyear made his discovery of vulcanisation process in 1839 and patented in 1844. He found that heating a mixture of rubber and sulfur generated products with improved properties than the raw rubber. Due to the increased demand for rubber and raised price caused by Civil War inflation, natives were exploited by traders to collect and cure rubber. There are thousands of trees were destroyed by improper tapping. The idea of planting and cultivating the Hevea rubber trees was proposed by Goodyear and Hancock. Henry Wickham, a coffee planter collected 70,000 seeds from Brazil to Kew Gardens for germination in 1876. About 2800 seeds were germinated and distributed to Sri Lanka, Singapore and Malaysia. Germinated seeds were send to Indonesia and India as well hereafter. Hevea seedlings were broadly distributed in Asia by 1880 (Subramaniam, 1987).

Extensive of experiments were carried out in between 1880 and 1900 on rubber plantation but the actual production was small. At this point, an important step in the growth of rubber industry was attributed to Henry N. Ridley in 1890. He developed an effective and economic method to obtain latex from latex vessel of Hevea tree by slicing the barks without injuring the trees, which is called "tapping". This method produced more latex and caused lesser damage compared to the practice of South American which cutting into the bark. Jon Perkins discovered the use of acid to coagulate latex and produce sheets dried in smoke in 1899. The pneumatic tire was invented by John Dunlop in 1888 has led to the thriving demand for rubber with the commencement of the motoring era early in the 20th century (Hurley, 1981). Plantation rubber production in Asia grew promptly and surpassed the wild rubber production from Brazil by about 1913. Southeast Asia retains the major natural rubber-producing region henceforth. Malaysia was the biggest producer, followed by Indonesia and Thailand in 1983. In recent years, the leading countries account for natural rubber production are Thailand, Indonesia, Vietnam, China, India and Malaysia.

Competition from synthetic rubber compelled the natural rubber industry to implement a more enterprising posture in 1964. Shortcomings in natural rubber focused on presentation standards and the traditional system of visual grading. Standard Malaysian Rubber (SMR) Scheme announced in Malaysia and later employed by other producing countries, aims to eradicate these two disadvantages of natural rubber. SMR are natural rubbers graded by technical specifications, not according to the conventional visual standards. Example of SMR are listed in Table 2.7.

Table 2.7: Standard Malaysian Rubber Specification

Parameter	TSR CV		TSR L	TSR 5		TSR 10		TSR 20	
	SMR CV50	SMR CV60	SMR L	SMR 5	SMR GP	SMR 10	SMR 10CV	SMR 20	SMR 20CV
Dirt (max % wt on 40 µm mesh)	0.02	0.02	0.02	0.05	0.08	0.08	0.08	0.16	0.16
Ash (max % wt)	0.50	0.50	0.50	0.60	0.75	0.75	0.75	1.00	1.00
Nitrogen (max % wt)	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Volatile matter (max % wt)	0.80	0.80	0.50	0.80	0.80	0.80	0.80	0.80	0.80
Plasticity retention index (min %)	60	60	60	60	50	50	50	40	40

Association of Natural Rubber Producing Countries (ANRPC) was established comprising Malaysia, Indonesia, Singapore, Sri Lanka, Thailand, and Vietnam in 1970. This association provides an inter-governmental forum for consideration of natural rubber producers to bring about a stable price structure. There are total 13 members of countries participate as members in ANRPC nowadays, cooperate together to analyse policies and formulate suitable strategies for protecting interests of natural rubber producers.

2.4.2 Usage of natural rubber

Natural rubber is commonly utilised in applications which require capabilities of wear and heat resistance. Majority of natural rubber is used in vehicle tires including race cars, buses, and aircrafts. It is also used in engineering applications, such as anti-vibration mounts, drive couplings, conveyor belts, bearings, rubber bands, and adhesives. Natural rubber can also be found in housewares and stationeries, for instance, rubber hoses, ducting, foam mattresses, battery boxes, bottles, and erasers. It can be applied in flooring of gym rooms, kitchens, animal shelters, and playgrounds as well for anti-slipping and waterproof properties. Natural rubber also involved in sport and child's products such as the manufacturing of footballs, basket balls, toys, and pacifiers. Personal items for examples, clothing, and shoe soles can find the applications of natural rubber. Others usage including medical devices, gloves, and airbags.

Natural rubber is also used in coatings applications such as tablet coatings (Panrat et al., 2012), microelectronic coatings (Ayche et al., 2016) and so on due to its high elasticity, high tensile strength, and ease of film-forming properties. Natural rubber is utilised as modifier as well, such as toughening agent for epoxy resin to alter the brittleness of the epoxy matrix (Tan et al., 2013), bio-modifier for bitumen and asphalt to improve the quality of pavement, lengthen its service life, and reduce costs in maintaining road (Azahar et al., 2016).

2.4.3 Preparation of liquid epoxidized natural rubber

Epoxidized natural rubber (ENR) is a type of chemically modified the natural rubber. ENR can be prepared by converting a part of carbon-carbon double bonds into epoxide groups using peracetic acid or performic acid which is generally produced in-situ from the reaction between hydrogen peroxide with the corresponding acids (Hashim &

Ong, 2017). By monitoring the amount of peracetic or performic acids generated, the extent of epoxidation of natural rubber can be varied, forming products such as ENR10, ENR25, and ENR50 which contain 10%, 25%, and 50% of C=C bonds converted into epoxide groups respectively. Liquid epoxidized natural rubber (LENR), shorter chain ENR can be produced by the degradation of ENR. This low-molecular-weight ENR can be produced via mechanical breakdown with roll mill, photo-oxidation with UV radiation, or chemical-oxidative degradation (Rooshenass et al., 2016).

2.4.3.1 Chemical-oxidative degradation of natural rubber

Chemical oxidative degradation of ENR can be achieved using potassium peroxodisulphate, periodic acid, or potassium permanganate.

For chemical degradation which is initiated by potassium peroxodisulphate, ENR25 is first dissolved in solvent to form ENR solution in reaction vessel, then the potassium peroxodisulphate and disodium hydrogen phosphate aqueous solution is added drop-wise into the ENR solution. The reaction is held at 60 ˚C with constant mixing and flow of air pumped to the solution. The degradation process involves free radical mechanism. Potassium peroxodisulphate acts as a radical initiator, is activated thermally to convert persulfate into sulphate radical which is one of the strongest oxidising species. The carbon-carbon double bonds are attacked to break the ENR polymer chains (Rooshenass et al., 2016).

For degradation involving periodic acid, reaction of ENR solution with periodic acid is carried out at 30 °C with constant stirring mixture of them in reaction vessel. The amount of periodic acid could affect the degradation pathway. At low periodic acid concentration, degradation of rubber occurs only via the cleavage of C=C double bonds, whereas at higher amount, H^+ of periodic acid has higher tendency to attack and cleave the epoxide groups of the rubber (Rooshenass et al., 2018). Periodic acid is also used to degrade ENR in latex stage by Phinyocheep et al. and the chain scission is done through breaking of C=C bonds as well (Phinyocheep et al., 2005).

For degradation with potassium permanganate, potassium permanganate is first dissolved in water and acetic acid and then added into as prepared ENR solution in reaction vessel. The mixture is stirred constantly at room temperature for reaction to take place. Under alkaline condition, the cleavage of C=C double bonds results with formation of cis diols, but C=C cleavage via cyclic fragmentation process prevails under acidic condition. Epoxide groups are attacked by potassium permanganate as well but the consumption of double bonds predominates (Rooshenass et al., 2018).

Yusof et al. carried out the degradation of ENR using hydrogen peroxide and sodium nitrite as degrading agents with the presence of surfactant in latex stage. ENR latex is diluted in the presence of sodium dodecyl sulphate and then incubated at room temperature. After that, hydrogen peroxide and sodium nitrite in ratio 1:1 are added into the diluted latex. The reaction temperature is held at 338 K for 8 hours. Mild basic condition that is around pH 8 is the most favourable condition, providing the highest reduction in molecular weight of ENR compared to mild acidic and high basic condition. C=C double bonds is involved in the cutting of ENR chains. Alkene is epoxidized by peroxynitrite which is produced from reaction of hydrogen peroxide and sodium nitrite, then the epoxy ring is attacked by the in situ generated nitrite ion form chain scission (Yusof et al., 2021).

In general, chemical oxidative degradation methods are able to break down ENR effectively, however the amount of epoxide group preserved in the degraded product is relatively lower compared to photo-oxidative degradation, and there are contained significant amount of side products generated in the degraded ENR (Pejvak, 2017).

2.4.3.2 Photo-oxidative degradation of natural rubber

Degradation of ENR can be achieved by photo-oxidation using UV radiation with wavelength of 365nm. The ENR is first dissolved in solvent in a beaker, then the ENR solution is located under a UV lamp to be irradiated with UV light. The solution is stirred by mechanical stirring during the UV irradiation. This degradation process involve free radical mechanism. The free radicals are created to attack the C=C double bonds or abstract the allylic hydrogen in the presence of oxygen. The epoxide group was not affected significantly during the UV irradiation, they are not involved in the chain scission reaction. The cleavage occurs predominantly via the C=C double bonds. This method is reported to produce ENR without much contaminant and able to yield smaller fraction LENR which retain substantial amount of epoxide groups. UV irradiation is preferred when the purpose on preserving the epoxide group is concerned while breaking down the ENR (Rooshenass et al., 2016, 2018).

2.4.4 Application of liquid epoxidized natural rubber

Liquid epoxidized natural rubber (LENR) was used for surface coating application. Kwanming et al. produced a liquid natural rubber by degradation of natural rubber latex with hydrogen peroxide and cobalt acetylacetonate then epoxidation was carried out by reacting with formic acid and hydrogen peroxide to obtain epoxidized liquid natural rubber (ELNR). Acrylated epoxidized liquid natural rubber was prepared by reaction of acrylic acid and ELNR in the ratio of 2:1. Surface coatings were formed by exposing the mixture of acrylated ELNR, crosslinker and photoinitiator under UV irradiation. The UV cured coatings showed highest hardness at 4H and resistance to 2% H_2SO_4 and distilled water for more than 24 hours (Kwanming et al., 2009).

Ooi and companions using LENR to coat the oil palm ash (OPA) in the OPA reinforced natural rubber composites. LENR50 were mixed with OPA particles and stirred using a mechanical stirrer followed by ultrasonic vibrator to ensure OPA particles were coated by LENR. LENR-coated OPA were dried in oven at 60 ˚C. Then, they were loaded in natural rubber composites. The LENR-coated OPA filled natural rubber composites exhibited improved ageing resistance than non-coated OPA filled natural rubber composites with higher retention of tensile strength and elongation at break value. LENR-coated OPA natural rubber composites also owned a higher thermal stability than non-coated one (Ooi et al., 2014).

LENR was used as toughening agent for composites, blends or prepolymers such as epoxy resin, plastic, and polyester. Kargarzadeh et al. utilised liquid natural rubber (LNR) and LENR to toughen the unsaturated polyester resins (UPRs). Natural rubber and epoxidized natural rubber was undergone photochemical degradation in the presence of visible light to produce LNR and LENR. LNR and LENR were mixed with UPRs, the mixture was cured at ambient temperature after introducing and mixing the initiator. Both rubber-modified resins presented improved tensile strength, impact strength, and fracture toughness. LENR-modified UPR showed greater enhancement in mechanical properties compared to LNR-modified UPR (Kargarzadeh et al., 2015).

Radhakrishnan Nair et al. used LENR to blend with polyvinyl chloride (PVC) to modify the impact strength. LNR was produced in different molecular masses which categorised into low-molecular mass LNR (L-LNR) and high-molecular mass (H-LNR) by photochemical degradation of natural rubber in presence of ultraviolet irradiation or sunlight. ELNR was synthesised by epoxidation of LNR using glacial acetic acid and hydrogen peroxide to obtain 10, 20, 30, 40, and 50 mol% of epoxidation. A series of blends of PVC and ELNR with the presence of thermal stabilizer and solvent were dried under vacuum after magnetic stirring. The impact modification was greater in the L-

ELNR blends than H-ELNR blends considering the better dispersion and smaller domain size of L-ELNR (Radhakrishnan Nair et al., 2009).

LENR was also used in the formulation of solid polymer electrolyte. Rahman and companions synthesised an electrolyte film containing PVC, LENR5, ethylene carbonate blends with lithium perchlorate as the dopant salt. ENR50 was degraded under irradiation of UV light to produce low molecular weight ENR50. PVC was dissolved in tetrahydrofuran (THF) followed by adding of LENR50 and stirred to form homogenous solution. After lithium perchlorate was dissolved in ethylene carbonate and THF, the solution was mixed into the as prepared mixture. The films with different concentration of lithium perchlorate were obtained after THF solvent was evaporated off under fume hood and subsequently in vacuum oven of the PVC, LENR50, and EC were miscible and blended well to from good homogeneity and smooth surfaces. Micro-pores assists the mobility of ions in the system complexes and thus enhancing the ionic conductivity. Electrolyte with 30 wt% of lithium perchlorate exhibited the highest ionic conductivity (Rahman et al., 2011).

2.5 Scope of study

The present study focused on the use of natural rubber derivative as a sustainable raw material in the formulation of two types of surface coatings, namely epoxy and alkyd coatings.

i. Production of low molecular weight liquid epoxidized natural rubber (UV-ENR) via ultraviolet treatment, followed by detailed characterization of the product to study the chemical structure, molecular weight and epoxide content after UV treatment.
ii. Development of epoxy coatings from UV-ENR with conventional hardener, PETMP as well as with green hardener, tannic acid, separately. The epoxy coatings with different UV-ENR: hardener ratios were prepared and the corresponding film properties were investigated which include physicochemical properties, thermal stability, as well as degradability.
iii. Synthesis of alkyd using liquid ENR to serve as polyol during the polyesterification. Different proportions of the rubber were included in the synthesis to evaluate the effect of having the rubber as a component in the alkyd. Resultant alkyds were mixed with reactive diluent, crosslinker and UV photoinitiators to form UV curable coating mixtures. Physicochemical properties, thermal stability, and drying time of UV-cured rubber-based alkyd films were investigated.
iv. Series of characterization ranging from spectroscopies (FTIR and ^{1}H-NMR), thermal analyses (DCS and TGA), and chromatography (GPC) were carried out. Standard methods adopted from ASTM were used in characterising in the film properties of the coatings, and this include pencil hardness, film adhesion, water, solvent and chemical resistance tests. Biodegradation test via soil/compost burial method were carried out on some of the coatings as well.

CHAPTER 3: METHODOLOGY

3.1 Materials

Epoxidized natural rubber 25, ENR25 and liquid epoxidized natural rubber, LENR50 were kind gifts from Malaysian Rubber Board. The number 25 and 50 indicate the percentage of epoxidation of the rubber. Palm oil used in this work was sponsored by Kuala Lumpur Kepong Berhad Malaysia (KLK).

Pentaerythritol tetra(3-mercaptopropionate) (PETMP) and bisphenol A diglycidyl ether (DGEBA), sodium chloride (NaCl), deuterated chloroform ($CDCl_3$), potassium hydroxide (KOH), and trimethylolpropane triacrylate (TMPTA) were obtained from Sigma Aldrich (USA). Tannic acid was obtained from Chemiz private limited (Malaysia). N,N-dimethylbenzylamine (DMBA) and styrene obtained from Sigma Aldrich (Germany). Tetrahydrofuran (THF) and sodium hydroxide (NaOH) were obtained from Friendermann Schmidt (Australia). Methanol (MeOH) and toluene were purchased from Kofa Chemical Works private limited (Malaysia), glycerol from Systerm, Classic Chemicals Sdn Bhd (Malaysia). Hydrochloric acid 37% (HCl) and methyl ethyl ketone (MEK) were obtained from RCI Labscan (Thailand). Phthalic anhydride and maleic acid were obtained from Merck (Germany). Benzophenone was obtained from Sigma Aldrich (China), and 1-hydroxycyclohexyl phenyl ketone (Irgacure 184) from Sigma Aldrich (Italy). All the chemicals were used as received.

Organic planting soil and bioorganic compost with tradename Premium Baba Super 10 and Agrostar, respectively are commercially available. Premium Baba Super 10 organic planting soil contains burnt soil, base fertiliser, coco peat, river sand, burnt husk, rich humus, charcoal powder, professional grade peat, added calcium and clay beaker.

Bio-organic compost is rich in plant based organic matter, bio-silica, Bacillus strains and various macro and micronutrients (total calcium 8.50%, magnesium 3.50%, nitrogen 3.00%, potassium 2.00%, phosphate 1.10%, sulphur 0.04%, boron 0.02%, iron 6770.00 ppm, zinc 31.00 ppm, manganese 21.20 ppm, copper 11.40 ppm, chloride 0.90%, citric acid 10.00%).

3.2 Preparation of low molecular weight ENR25

5 wt % of ENR25 solution was prepared by dissolving ENR25 in THF at ambient temperature. 100 g of 5 wt% ENR25 solution was placed in a beaker and irradiated with UV light for a total duration of 2, 4 and 6 hours with constant stirring. UV light source is from ELC-4001 UV Flood System which bear a 400W lamp that irradiate UV-A light at wavelength 365nm and intensity of 125 mW/cm^2 (Figure 3.1). Small amount of THF was added into the mixture periodically throughout the UV irradiation to ensure the volume of the mixture remains approximately constant. After fixed UV irradiation period, the mixture was transferred to a petri dish, and allowed to dry in fume hood overnight, followed by further drying in oven at 60 ˚C until constant weight was obtained. UV-irradiated ENR25 are henceforth labelled as 2 hours UV-ENR25, 4 hours UV-ENR25 and 6 hours UV-ENR25, with the number of hours in the name reflecting the duration of the UV treatment.

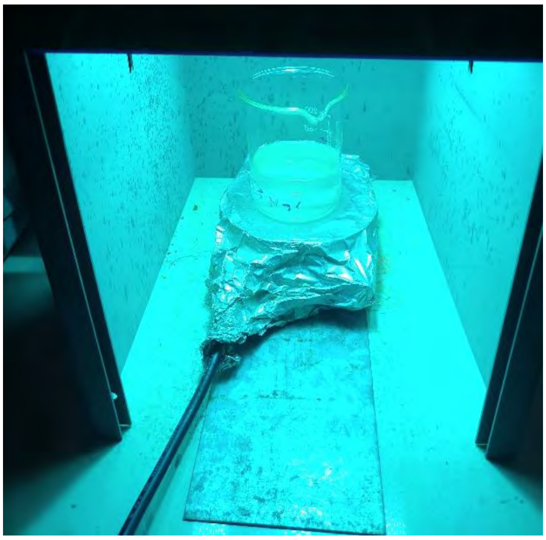


Figure 3.1: UV irradiation of ENR25 in THF solution

3.3 Characterization of UV-ENR25

3.3.1 Fourier-transform infrared (FTIR) spectroscopy

Rubber samples (ENR25, 2 hours UV-ENR25, 4 hours UV-ENR25 and 6 hours UV-ENR25) were dissolved in THF to form rubber solution before they were applied on KBr cell. The films were then blow-dried to remove the THF solvent in the films. Films were scanned using Perkin Elmer RX1 FTIR spectrometer at resolution of 4 cm^{-1}. The scans were performed from wavenumber 400 to 4000 cm^{-1}.

3.3.2 Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy

Rubber samples were dissolved in deuterated chloroform, $CDCl_3$ in the presence of tetramethylsilane, TMS. The samples were analysed using JEOL JNM-GSX 270 NMR spectrometer. Deuterium in $CDCl_3$ locks the magnetic field while TMS functioned as the internal standard to lock the signal at 0 ppm.

3.3.3 Gel permeation chromatography (GPC)

Rubber samples were dissolved in THF to a concentration of 0.5 wt % for GPC analysis. After samples were filtered via polytetrafluoroethylene film with pore size of 0.45 µm, about 100 µL of samples were then injected into a Tosoh HLC-8320 gel permeation chromatography instrument. The flow rate applied was 0.8 mL/min, and two columns of TSKgel SuperMulltipore HZ-M were employed in the system. GPC instrument was calibrated using anionically polymerized polystyrene narrow standards which cover a number-average molecular weight range of 500 - 8,000,000 g/mol, with a dispersity of < 1.10.

3.3.4 Determination of epoxy equivalent

Epoxide values of rubber samples were obtained by back-titrating the rubber solutions with hydrochloric acid, a method adapted from (He et al, 2014). A fixed amount of rubber sample was dissolved in 30 mL of THF to form a sample solution. 20 mL of solution made up of 1:50 ratio of HCl: THF was then added into the sample solution and the mixture was stoppered and allowed to stand in the dark for 30 minutes. The mixture was then titrated with standardised KOH solution (in methanol). Blank determination was carried out on sample without any UV-ENR25. Measurement was carried out in triplicate set and the average value was reported.

Epoxide value was calculated by the following equation:

$$\text{Epoxide value}, mol/kg = \frac{(V_0 - V) \times N}{W} \tag{3.1}$$

V_0 is volume of standardised KOH solution used to titrate with HCl-THF solution of blank (mL)

V is volume of standardised KOH solution used to titrate with HCl-THF solution of sample (mL)

N is concentration of standardised KOH solution (mol/L)

W is dry mass of rubber sample (g)

KOH was standardised before titrating with samples mixtures. KHP was dried in oven at 110°C for 2 hours. 0.5 g of dried KHP was weighted into an Erlenmeyer flask and dissolved in 50-75mL of distilled water. The amount of KHP and distilled water used were recorded. 3 drops of phenolphthalein was added into the flask. The mixture was titrated to the first permanent appearance of pink with KOH solution (in methanol). Near the endpoint, KOH was added drop wise to determine the total volume accurately. Measurement was carried out in triplicate set and the average value was reported.

3.4 Preparation of epoxy coating (UV-ENR25/PETMP coating)

3.4.1 Preparation of UV-ENR25/PETMP coating mixture

6 hours UV-ENR25 was dissolved into THF and the concentration final solution was adjusted to 35 wt% which is the maximum rubber solubility with optimal viscosity for mixing. Coating mixtures were prepared by mixing PETMP (list of property is provided in Appendix A) and 35 wt% UV-ENR25 solution in THF solvent by using magnetic bars at ambient temperature. DMBA was added as catalyst to speed up the reaction between UV-ENR25 and PETMP and the amount introduced was set at 10 wt% of the amount of PETMP. The formulations of the coatings prepared are given in Table 3.1. Note that the amount of UV-ENR25 recorded in Table 3.1 is with respect to the amount of rubber content. Coating R100 was prepared to serve as control.

Table 3.1: UV-ENR25/PETMP coating formulations

Coatings	UV-ENR25/ wt%	PETMP/ wt%	Composition/ g		
			PETMP	UV-ENR25	DMBA
R80	80.00	20.00	0.39	1.57	0.04
R67	66.70	33.30	0.65	1.29	0.06
R57	57.00	43.00	0.82	1.10	0.08
R50	50.00	50.00	0.95	0.95	0.10
R43	43.00	57.00	1.08	0.81	0.11
R100	100.00	0	-	2.00	-

3.4.2 Treatment of mild steel panel

Prior to film application, mild steel panels were treated to remove any impurities covered on the surface meanwhile to minimize the effect of substrate during film property test. Oil or strains on the panels were cleaned off using toluene. After rubbing by paper towels, the remaining toluene was wiped off using acetone. Panels were rubbed by paper towels with acetone until the surfaces were toluene-free and dust-free. Finally, they were wiped dry and kept in desiccator prior to use.

3.4.3 Application and curing of UV-ENR25/PETMP coatings

Coating mixtures were mixed to homogeneity and then applied on mild steel panels or microscope plain glass slides using a bar coater with 50 µm gap. The use of different types of panels was depended on the test carried on the coatings. For instance, coating mixtures were coated on mild steel panels for hardness test and film adhesion test. For gel content test, water and chemical resistance test, coating mixtures were coated on glass panels. The coated mild steel and glass panels were then left to cure in thermal oven at 80 ºC for 24 hours. The coatings were left for room conditioning before the following tests were carried out on the films. Figure 3.2 shows diagrammatical flow on the preparation of UV-ENR25/PETMP coating.

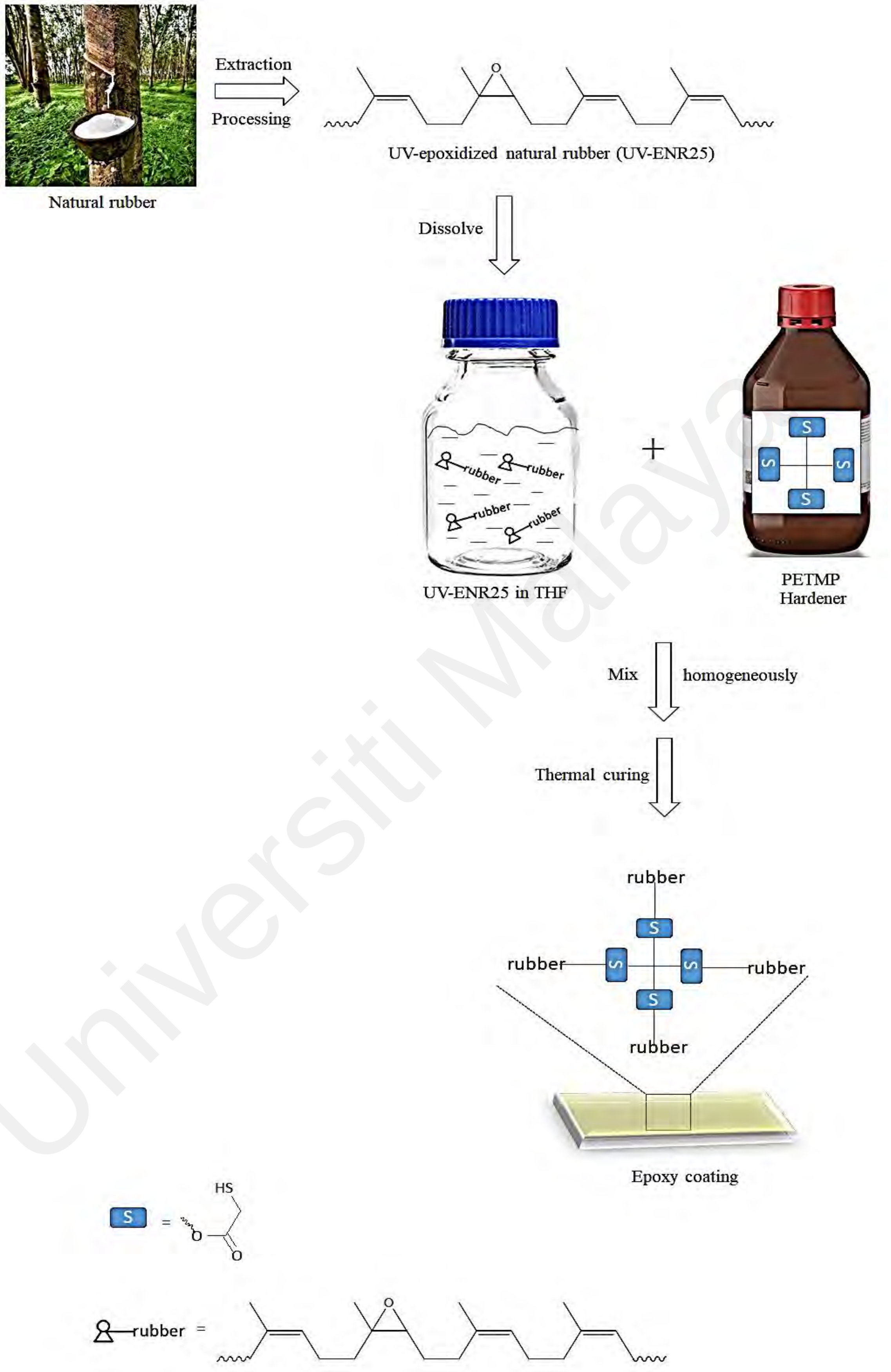


Figure 3.2: Diagrammatical flow on the preparation of UV-ENR25/PETMP coating

3.5 Characterization of cured epoxy coating (UV-ENR25/PETMP coatings)

3.5.1 Fourier-transform infrared (FTIR) spectroscopy

Cured coating and wet film before curing were scanned using Perkin Elmer RX1 FTIR spectrometer at resolution of 4 cm^{-1}. The scans were performed from wavenumber 400 to 4000 cm^{-1}.

3.6 Determination of film properties of cured epoxy coatings (UV-ENR25/PETMP coating)

3.6.1 Gel content

Gel content analysis was carried out by using glass slides as substrates for coatings. Weight of empty glass slides and coated glass slides were measured and reported as W_1 and W_2, respectively. After coated glass slides were immersed in THF for 48 hours, the slides were removed and lightly tapped dry with lint-free paper towel to get rid of excess solvent on the surface of the coatings. The coatings were subsequently dried in vacuum oven at 60˚C for 48 hours and the final weight of the dried coated glass slides is reported as W_3. Five sets of data were collected for each coating sample. The percentage of gel content was calculated according to the following equation:

$$\text{Gel content } \phi, wt\ \% = \left(\frac{W_3 - W_1}{W_2 - W_1} \times 100\right)\% \tag{3.2}$$

where (W_3-W_1) is weight of dried coating remains after immersion

(W_2-W_1) is initial weight of coating before immersion

3.6.2 Pencil hardness test (PHT): ASTM D3363

Pencil hardness test was conducted according to ASTM D3363 to measure the film hardness of coatings. Mild steel panels coated with coatings were placed on a horizontal surface. Pencils with different hardness grades were held 45˚ on coating surfaces in Wolff-Wilborn pencil hardness kit. The kit was pushed in a single stroke, away from the operator. The softest grade pencil used starts from 6B, and the highest being 6H. The hardest pencil grade that was able to scratch the film was reported. Before holding the wood pencils into the kits, they were sharpened to emerge the leads by a sharpener. Then, they were held at an angle of 90° to the abrasive paper, and the leads were rubbed against the paper until flat, smooth and circular cross sections were obtained. The test was repeated four times for each coating formulation.

6B – 5B – 4B – 3B – 2B – B – HB – F – H – 2H – 3H – 4H – 5H – 6H

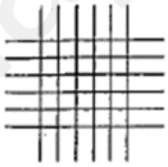
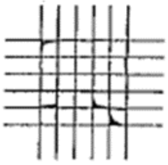
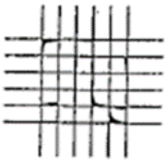
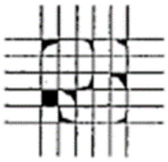
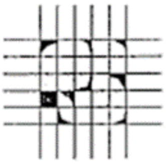
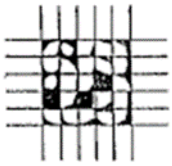
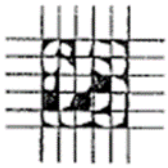
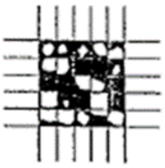
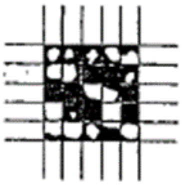
Softer Harder

Figure 3.3: Pencil hardness scale

3.6.3 Film adhesion test: ASTM D3359

Film adhesion test was conducted on coated mild steel panels according to ASTM D3359, method B – cross-cut tape test. Grids formed by 11 vertical and horizontal lines were carved on coatings using a blade. After the cuts were made, any detached flakes were removed from the coating surfaces. Adhesion tapes were then applied on the grids and rubbed firmly to make maximum contact with films. The colour under the tape was used to determine whether there was good contact between tape and film. The tapes were then removed in single strokes as close to an angle of 180° as possible. The grid areas were inspected and percentage of coatings peeled off from the grid areas were recorded. The test was repeated eight times for each coating. The classification of adhesion test results is shown in Table 3.2.

Table 3.2: Classification of adhesion test results

Classification	Coating area removed / %	Surface of cross-cut from which flaking has occurred and adhesion range by percent
5B	0	
4B	< 5	
3B	5 - 15	 
2B	15 - 35	 
1B	35 - 65	 
0B	> 65	

3.6.4 Solvent resistance test: ASTM D5402

Solvent resistance test was conducted on coatings by using mild steel panels as substrates. The test method was adopted from ASTM D5402. The thickness of mild steel panels and coated panels were recorded. Coated surfaces were ensured that were free of dust and impurities prior the test. A cotton cloth was dampened with MEK solvent until a dripping condition. The solvent-saturated cloth was double rubbed 25 times on the coating surface by using an index finger with moderate pressure. A double rub includes one forward motion away from operator and one back motion towards the operator. The thickness after rubbing with solvent was recorded by using a micrometer screw gauge and the change of film thickness was calculated. The test was repeated eight times for each coating.

3.6.5 Water resistance test

Water resistance test was conducted on coated glass slides based on method adapted from ASTM D1647. Coated glass slides were immersed in distilled water separately for 24 hours at ambient temperature. After the coated glass slides were removed from the distilled water, the coating conditions were observed and evaluated. If whitening appeared, the coated glass slides were left dried in room condition. The durations needed for whitening disappeared were recorded.

3.6.6 Alkaline resistance test

For alkaline resistance test, the method used was adapted from ASTM D1647. Coated glass slides were immersed in NaOH aqueous solution with concentration 30g/L. After an hour of immersion, the coated glass slides were removed from the separate containers filled with NaOH solution. The film conditions were inspected and evaluated whether there were permanent damages such as blistering, discolouration, film removal and dissolution.

3.6.7 Acid resistance test

Acid resistance test was carried out on coated glass slides by adapting a method from the work of K.P. Somani and companions (Somani et al., 2003). The coated glass slides were immersed in 0.1M HCl aqueous solution separately. HCl solution was preheated at 80˚C and the temperature was remained constant throughout the immersion. After 1 hour, the coated glass slides were removed from acid solution and the film conditions were evaluated.

3.6.8 Saltwater resistance test

Saltwater resistance test was conducted in a way similar to method described on Section 3.6.6. The coated glass slide were immersed in preheated 5% w/w NaCl aqueous solution and the temperature was maintained at 80˚C during the 1 hour immersion. The coated glass slides were then taken out from NaCl solution. The film conditions were observed and evaluated.

3.6.9 Contact angle measurement

Contact angle measurement was conducted on coated glass slides using sessile drop method with Kruss G-23 contact angle analyser at room temperature. The air velocity was taken cautiously to avoid influence on the result of measurement. Liquid droplet chosen to deposit on the coating surfaces was deionised water by a micrometer syringe. Contact angles of six different regions were taken for each coating and the average values were measured.

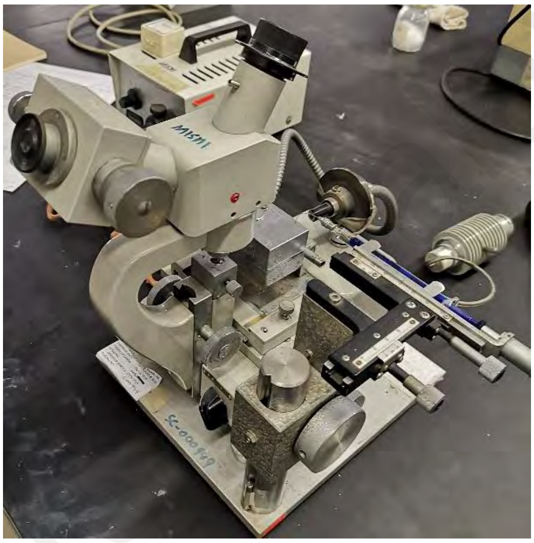


Figure 3.4: Kruss G-23 contact angle analyser

3.6.10 Thermal gravimetric analysis (TGA)

Coatings were scraped off from the glass panels to run for TGA analysis after they were cured and undergone room conditioning. Coatings were scraped carefully to avoid any contaminant such as flakes of glass panels that could affect the accuracy of analysis. Perkin Elmer (TGA 6) thermogravimetric analyser was used to obtain the thermograms of coatings. Scanning of coatings were conducted under N_2 atmosphere from 50°C to 900°C at heating rate of 20°C/min.

3.6.11 Differential scanning calorimetry (DSC)

Samples of epoxy coatings for DSC analysis were obtained in similar way as the samples for TGA analysis. About 8-10 mg of coating samples were put into aluminium sample pans and sealed with the matched aluminium caps. The thermogram of coatings were obtained using DSC machine model TA DSC-Q20. After the thermal histories, if any were eliminated, the glass transition temperature of coating was obtained by scanning them from -60°C to 120°C at heating rate 20°C/min under N_2 atmosphere.

Figure 3.5: Heat flux DSC with single furnace which accommodate both sample pans

3.7 Preparation of epoxy coating (UV-ENR25/tannic acid coating)

3.7.1 Preparation of UV-ENR25/tannic acid coating mixture

4 hours UV-ENR25 was dissolved in THF solvent and the final concentration to 10 wt%. To prepare tannic acid solution, 10g of tannic acid powder was first mixed into 90g of THF and refluxed in THF for 3.5 hours at 55-60 ˚C with constant stirring to enhance the solubility of tannic acid. Tannic acid solution was then filtered to remove the remaining undissolved powder. The final concentration of tannic acid solution was adjusted to 20 wt%.

Coating mixtures were prepared by mixing 4 hours UV-ENR25 solution and tannic acid solution using magnetic bars at ambient temperature. The formulations of coating mixtures prepared as showed in Table 3.3. Noted that the amount of UV-ENR25 recorded in Table 3.3 is with respect to the amount of rubber content and dry weight of tannic acid. R100 and T100 were served as control coatings. R100 was made up from solely UV-ENR25 solution whereas T100 formulated with tannic acid solution only. Coating T20-X5 and T20-X9 were formulated with the same ratio of UV-ENR25: tannic acid as in coating T20, but with addition of DGEBA. Small amount of DGEBA was introduced into coating mixture with intention to enhance the extent of crosslinking in coating films.

Table 3.3: UV-ENR25/Tannic acid coating formulations

Coating	UV-ENR25/ wt%	Tannic Acid/ wt%	DGEBA/ wt%
T10	90	10	-
T20[a]	80	20	-
T35	65	35	-
T50	50	50	-
T65	35	65	-
T80	20	80	-
R100	100	0	-
T100	0	100	-
T20-X5[a]	76	19	5
T20-X9[a]	73	18	9

[a] *Ratio of tannic acid: UV-ENR25 is constant*

3.7.2 Treatment of mild steel panel

Prior to film application, mild steel panels were treated to remove any impurities covered on the surface meanwhile to minimize the effect of substrate during film property test. Oil or strains on the panels were cleaned off using toluene. After rubbing by paper towels, the remaining toluene was wiped off using acetone. Panels were rubbed by paper towels with acetone until the surfaces were toluene-free and dust-free. Finally, they were wiped dry and kept in desiccator prior to use.

3.7.3 Application and curing of UV-ENR25/tannic acid coatings

Coating mixtures were mixed to homogeneity and then applied on mild steel panels or microscope plain glass slides using a bar coater with 50 μm gap. The use of different types of panels was depended on the test carried on the coatings. The coatings were left for room conditioning before the following tests were carried out on the films. Figure 3.6 shows diagrammatical flow on the preparation of UV-ENR25/Tannic acid coating.

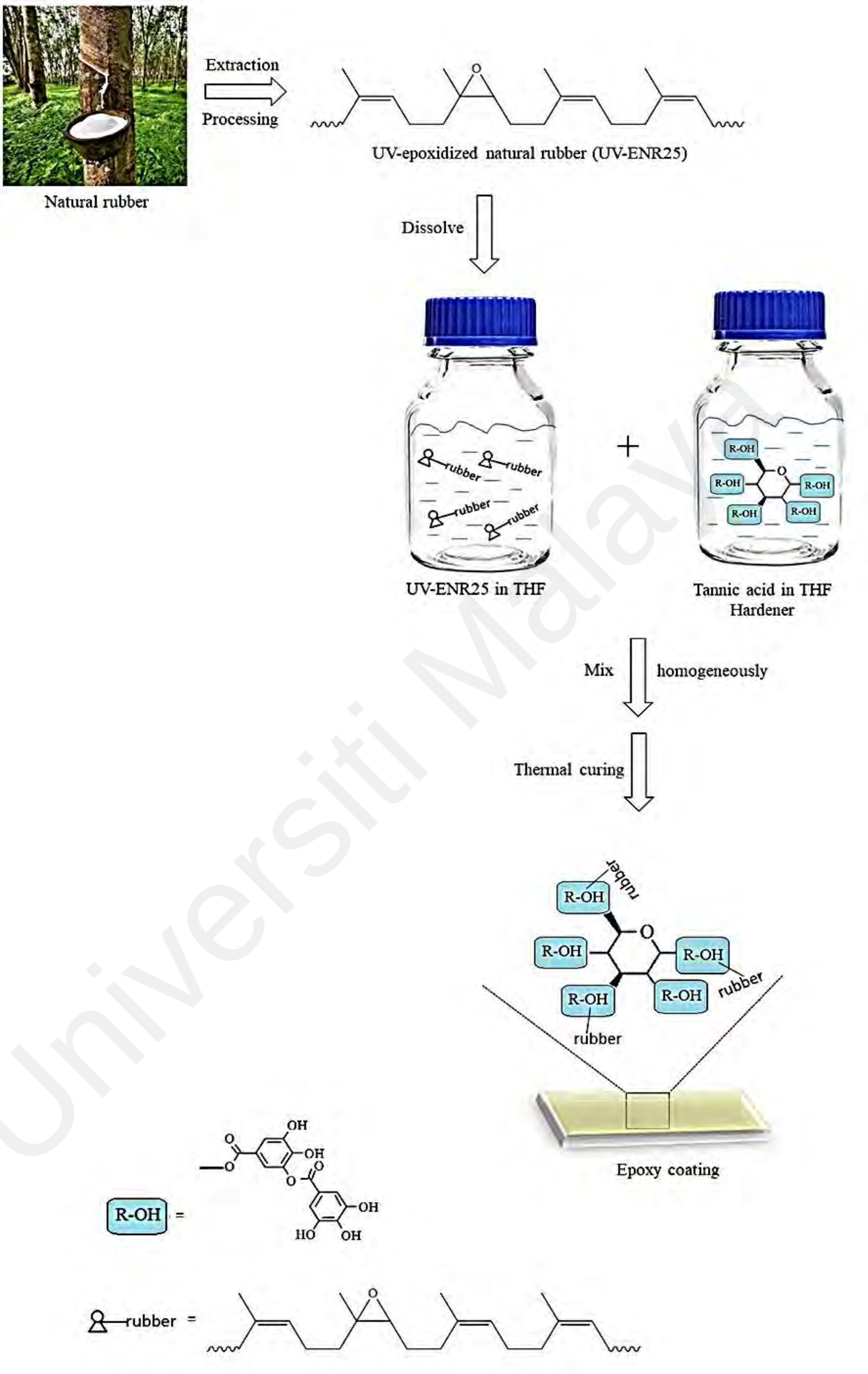


Figure 3.6: Diagrammatical flow on the preparation of UV-ENR25/Tannic acid coating

3.8 Characterization of cured epoxy coating (UV-ENR25/tannic acid coating)

3.8.1 Fourier-transform infrared (FTIR) spectroscopy

The chemical composition of cured coating was investigated by Perkin Elmer Spectrum 400 FT-IR/ FT-FIR spectrometer with resolution of 4cm^{-1} from 400 to 4000 cm^{-1}.

3.9 Determination of film properties of cured epoxy coatings (UV-ENR25/tannic acid coating)

3.9.1 Water resistance test: ASTM D870

Water resistance test was carried out on coated glass slide based on method adopted from ASTM D870. The coated glass slides were immersed 24 hours in a water tank which filled with distilled water. The distilled water was maintained at temperature 38 ± 1˚C and stirred with a mechanical stirrer throughout the test. After 24 hours, the coated glass slides were removed from distilled water and the film conditions were evaluated visually. If any defect happened, the coatings were placed in room condition and the time taken for coatings to return back original appearances were recorded.

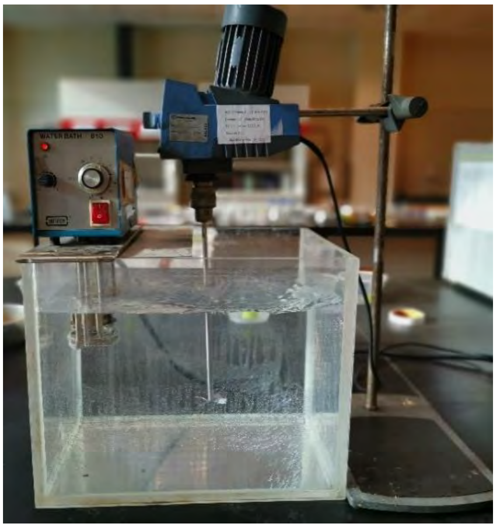


Figure 3.7: Distilled water-bath fixed with mechanical stirrer

3.9.2 Chemical resistance test: ASTM D543

Chemical resistance test was conducted on coatings prepared on glass slides according to the method adapted from ASTM D543. Weight of empty glass slides were first measured and reported as W_a. After the weight of coated glass slides were recorded as W_b, they were immersed in 10 wt% NaCl, 10 v/v% HCl and 10 wt% NaOH solution separately in room temperature for 7 days. Post immersion, coated glass slides were taken out from the solution, rinsed with distilled water and tap dried with paper towel. Then, the coated glass slides were dried thoroughly in vacuum oven until constant weight was gained. The final weight of dried coated glass slides were reported as W_c. The test was repeated four times for each coating. The percentage of weight change was calculated by following equation:

$$\text{Weight change}, wt\% = [\left(\frac{W_c - W_a}{W_b - W_a} \times 100\right) - 100]\% \tag{3.3}$$

where (W_c-W_a) is weight of dried coating remains

(W_b-W_a) is initial weight of coating before immersion

3.9.3 Contact angle measurement

Contact angle measurement was conducted on coated glass slide using sessile drop method. Deionised water was deposited onto surface of coatings by micrometer syringe. Kruss Easy Drop DSA 15E contact angle goniometer was used to measure the contact angle of both side of the drop.

3.9.4 Biodegradability test

Biodegradability test was carried out based on soil burial method for both indoor and outdoor setup. Test was conducted on coated glass slides. The weight of empty glass slides and coated glass slides were measured and reported as W_x and W_y respectively.

Indoor soil burial method was adapted from (Di Franco et al., 2004; Maran et al., 2014; Sharma et al., 2014). Soil used in the indoor biodegradability experiment was commercially available. It was made up from the mixture of bio-organic compost and organic planting soil in the ratio of 1:4. Before the beginning of test, soil mixture was hydrated with distilled water to provide it humidity. Then, the soil mixture was distributed roughly evenly into series of plastic boxes with dimensions 165mm × 115mm × 70mm. Six sets of coatings were prepared for each formulation. One set of coatings included three pieces of coated glass slides. A total of three coated glass slides with same formulation were buried into each plastic box with a fixed distance of separation. Coatings with different formulations were buried in different boxes. The plastic boxes were kept in room temperature without covering it in order to allow air exposure. The soil mixture was lightly hydrated with distilled water without extreme bias for all boxes every alternate day. External factors surrounding the experimental sets were keep constant as best as possible for each coating setup to avoid their effects on the rate and extent of biodegradability which affect the accuracy of result. These factors include humidity, soil fertility, temperature of soil, oxygen accessibility and so on (Eskander & Saleh, 2017).

After 2 weeks of burial, one set of coated glass slides of each formulation were taken out from the boxes and cleaned cautiously with distilled water. Next, the coated glass slides were dried in the vacuum oven until constant weight was gained. The weight of dried coated glass slides was measured and reported as W_z. The degree of degradation was evaluated by measuring the percentage of weight loss in coating which was calculated by the following equation:

$$\text{Weight change}, wt\% = [\left(\frac{W_z - W_x}{W_y - W_x} \times 100\right) - 100\,]\% \qquad (3.4)$$

where $(W_z\text{-}W_x)$ is weight of dried coating remains after burial

$(W_y\text{-}W_x)$ is initial weight of coating before burial

Another set of coated glass slides of each formulation were removed out from the soil after every 2 weeks. Similar procedures and measurement were done on the coatings. The test was conducted in a 3-month-period. A petroleum-based epoxy coating which is commercially available served as a control in this test.

Figure 3.8: Indoor set of soil burial method of biodegradability test

Outdoor soil burial method was adapted according to method from X. Yang and companions (Yang et al., 2015). The coated glass slides were buried in an empty grass field which provided an open natural environment for coatings to undergo their biological fate in a tropical climate. The burial depth for all coated glass slides was about 11.5 to 12.5 cm. At every fortnight interval, one set of coatings of all formulation were removed out by scrapping the soil with a hand shovel carefully to avoid damaging the coated glass slides. Next, the coated glass slides were gently cleansed with distilled water to eliminate the soil and/or dust from the coating. The operational procedure and calculation were conducted by same method as those in indoor soil burial method. Three sets of data were collected for each coating formulation in each burial interval. The surrounding condition of open environment hardly be controlled but it unpreventably becomes the factor affecting the degradation rate, thus the meteorological data of the 3-month burial period is presented in Table 3.4 to be referred.

Figure 3.9: Outdoor soil burial method of biodegradability test

Table 3.4: Meteorological data of the 3-month burial period (Sep 2019-Nov 2019)

	Sep 2019		Oct 2019		Nov 2019	
	Range	Average	Range	Average	Range	Average
Temperature / ˚C	23-35	29	23-34	27	23-35	27
Humidity / %	44-100	79	49-100	86	49-100	84
Rainfall / mm	-	125 (22 rain days)	-	477 (31 rain days)	-	243 (30 rain days)

Retrieved from meteorology website of "visualcrossing" and "timeanddate".

The photographs of coating surface images throughout both indoor and outdoor biodegradation process were captured using Leica triple camera with a main camera came with f/1.8 aperture and 40 megapixels.

3.9.5 Other tests:

Other tests carried out on the coatings are like those carried out in Section 3.6, and they include:

(a) Gel content (Section 3.6.1)
(b) Pencil hardness test (Section 3.6.2)
(c) Film adhesion test (Section 3.6.3)
(d) Solvent resistance test (Section 3.6.4)
(e) Thermal gravimetric analysis (Section 3.6.10)
(f) Differential scanning calorimetry (Section 3.6.11)

3.10 Characterization of LENR50

3.10.1 Fourier-transform infrared (FTIR) spectroscopy

The chemical composition of rubber sample was investigated by Perkin Elmer Spectrum 400 FT-IR/ FT-FIR spectrometer with resolution of 4cm^{-1} from 400 to 4000 cm^{-1}.

3.10.2 Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy

Rubber samples were dissolved in deuterated chloroform, $CDCl_3$ in the presence of tetramethylsilane, TMS. The samples were analysed using JEOL JNM-GSX 270 NMR spectrometer. Deuterium in $CDCl_3$ locks the magnetic field while TMS functioned as the internal standard to lock the signal at 0 ppm.

3.11 Preparation of LENR50-alkyd resins

3.11.1 Alkyd resins formulation

Alkyd resins were made up from palm oil, glycerol, phthalic anhydride (PA), maleic acid (MA) and degraded ENR50. Since the amount of rubber needed in the alkyd synthesis is high, and there is also a need for high concentration of epoxide group in the rubber, the alkyd synthesis was carried out using oxidatively degraded ENR50 (henceforth referred to as LENR50). The formulation of each alkyd resins is listed in Table 3.5 (100PA), 3.6 (20MA), 3.7 (5R), 3.8 (10R), 3.9 (15R), and 3.10 (10R10MA). Alkyds 100PA and 20MA served as controls and they were formulated in the absence of LENR50. Between the two controls. 20MA have additional unsaturation from the incorporation 20% of maleic acid. 5R, 10R, and 15R are codenames for alkyds synthesised with 5 wt%, 10 wt%, and 15 wt% of LENR50 respectively, 10R10MA referred to alkyd formulated with 10 wt% of LENR50 and 10% of maleic acid. In the alkyd syntheses, palm oil was used as the source of fatty acids, glycerol as the main polyol, PA and/or MA were diacids, and LENR50 as an alternative polyol. Calcium hydroxide, $Ca(OH)_2$ was introduced as catalyst. Percentage oil length of all the alkyds were formulated at about 38 – 43% which fall under the short oil length alkyd category. The summarised composition of alkyd resins is given in Table 3.11, and example calculation of parameters related to alkyd synthesis is shown next.

Table 3.5: Formulation of 100PA

Components	Mass / g	Molecular weight / g/mol	Molarity	Number of equivalent	
			Mole of molecule / mol	Mole of OH	Mole of COOH
Palm oil	152.25	847.04	0.18	0.54	0.54
Glycerol	83.45	92.10	0.91	2.72	
Phthalic anhydride	127.50	148.10	0.86		1.72
Maleic acid	0	116.10	0		0
Total (g)	363.20		1.95	3.26	2.26

Table 3.6: Formulation of 20MA

Components	Mass / g	Molecular weight / g/mol	Molarity	Number of equivalent	
			Mole of molecule / mol	Mole of OH	Mole of COOH
Palm oil	152.25	847.04	0.18	0.54	
					0.54
Glycerol	83.45	92.10	0.91	2.72	
Phthalic anhydride	102.40	148.10	0.69		1.38
Maleic acid	20.10	116.10	0.17		0.34
Total (g)	358.20		1.95	3.26	2.26

Table 3.7: Formulation of 5R (5 wt% LENR50)

Components	Mass / g	Molecular weight / g/mol	Molarity	Number of equivalent	
			Mole of molecule / mol	Mole of OH	Mole of COOH
LENR50	18.25			0.12	
Palm oil	152.25	847.04	0.18	0.54	
					0.54
Glycerol	79.76	92.10	0.87	2.60	
Phthalic anhydride	127.50	148.10	0.86		1.72
Maleic acid	0	116.10	0		0
Total (g)	377.76		1.91	3.26	2.26

Table 3.8: Formulation of 10R (10 wt% LENR50)

Components	Mass / g	Molecular weight / g/mol	Molarity	Number of equivalent	
			Mole of molecule / mol	Mole of OH	Mole of COOH
LENR50	38.00			0.25	
Palm oil	152.25	847.04	0.18	0.54	
					0.54
Glycerol	75.77	92.10	0.82	2.47	
Phthalic anhydride	127.50	148.10	0.86		1.72
Maleic acid	0	116.10	0		0
Total (g)	393.52		1.86	3.26	2.26

Table 3.9: Formulation of 15R (15 wt% LENR50)

Components	Mass / g	Molecular weight / g/mol	Molarity	Number of equivalent	
			Mole of molecule / mol	Mole of OH	Mole of COOH
LENR50	59.50			0.39	
Palm oil	152.25	847.04	0.18	0.54	
					0.54
Glycerol	71.43	92.10	0.78	2.33	
Phthalic anhydride	127.50	148.10	0.86		1.72
Maleic acid	0	116.10	0		0
Total (g)	410.68		1.82	3.26	2.26

Table 3.10: Formulation of 10R10MA (10 wt%LENR50, 10% maleic acid)

Components	Mass / g	Molecular weight / g/mol	Molarity	Number of equivalent	
			Mole of molecule / mol	Mole of OH	Mole of COOH
LENR50	37.50			0.25	
Palm oil	152.25	847.04	0.18	0.54	
					0.54
Glycerol	75.77	92.10	0.82	2.47	
Phthalic anhydride	114.50	148.10	0.77		1.55
Maleic acid	10.05	116.10	0.09		0.18
Total (g)	390.07		1.91	3.26	2.27

Table 3.11: Summary of alkyd resins compositions

Resins	LENR50 / wt% [a]	Palm oil / g [b]	Glycerol / portion	Phthalic anhydride / % [d]	Maleic acid / % [d]
100PA	0	P	G	100	0
20MA	0	P	G	80	20
5R	5	P	G-5R [c]	100	0
10R	10	P	G-10R [c]	100	0
15R	15	P	G-15R [c]	100	0
10R10MA	10	P	G-10R [c]	90	10

[a] *weight percentage with respect to expected yield*

[b] *weight of oil remained constant for all formulation, P*

[c] *weight of glycerol = (mole of OH contributed from glycerol in G - mole of epoxide contributed from LENR50) x molar mass of glycerol*

[d] *percentage of a diacid with respect to total percentage of all diacids*

Using 10R10MA as example for calculation:

Percentage oil length $= \frac{\text{Weight of oil } (g)}{\text{Total weight of alkyd } (g)} \times 100$ (3.5)

$= \frac{152.25}{390.07} \times 100$

= 39.03 %

Total water expected = [Mole of PA + (Mole of MA x 2)] x (3.6)

Molecular weight of H_2O (g/mol)

= [0.77 + (0.09 x 2)] x 18

= 17.10 g

Expected yield = Total charge of components (g) – total water expected (g) (3.7)

= 390.07 – 17.10

= 372.97 g

Weight percentage of LENR50 introduced based on expected yield (3.8)

$= \frac{\text{Weight of LENR50 } (g)}{\text{Weight of expected yield } (g)} \times 100$

$= \frac{37.5}{372.97} \times 100$

= 10.05 %

Percentage of unsaturation from MA based on total diacids (3.9)

$= \frac{\text{Number of COOH group equivalent of MA}}{\text{Total number of COOH group equivalent of MA+PA}} \times 100$

$= \frac{0.18}{0.18+1.55} \times 100$

= 10.04 %

3.11.2 Alkyd cooking procedure

Alkyds were cooked according to the formulation listed in Section 3.10.1. Each cook was divided into two stages, alcoholysis of palm oil into predominant mixture of monoglycerides and polycondensation between product in first stage with PA and/or MA. The first stage started with mixing palm oil, glycerol, and $Ca(OH)_2$ at 230˚C for 3 hours. The reaction mixture in reaction flask was actively stirred with an overhead stirrer, and its temperature was monitored closely using digital thermometer. The completeness of alcoholysis was verified by testing the miscibility of methanol with monoglyceride at volume ratio 3:1. The experimental setup for the alcoholysis part was shown in Figure 3.10.

LENR50 was dissolved in toluene at concentration of 15 wt%. After the alcoholysis process, the temperature of reaction mixture was cooled down to <150˚C. Then, the LENR50 solution and diacids were added gradually into the flask for the polycondensation process. The temperature was gradually increased to 220˚C and held constant throughout the synthesis. The experimental setup for polycondensation step is shown in Figure 3.11. In this stage, Dean-Stark trap was attached to collect and remove the water produced from the condensation, to avoid the reverse reaction and favour the forward equilibrium.

The extent of conversion of the synthesis was monitored by measuring the acid value of the mixture from time to time. The cooking was terminated when the acid value reach <10 % of the initial acid number. Initial acid number of alkyd was calculated theoretically using Eqn 3.10. Acid value of the sample was measured using AOCS Official Method Te 2a-64. Sample was weighed and transferred into a conical flask, followed by addition of 100mL of neutralized solvent (mixture of isopropanol and toluene in 1:1 ratio) and a few drops of phenolphthalein indicator. The mixture was stirred until alkyd sample was completely dissolved. The sample mixture was titrated with standardised NaOH- methanol solution until the end point achieved. The acid value was calculated using Eqn 3.11.

$$\text{Initial acid number} = \frac{56105.6\times\text{Number of COOH equivalent}}{\text{Weight of alkyd }(g)} \tag{3.10}$$

$$\text{Acid value} = \frac{\text{Volume of NaOH }(mL)\times\text{Normality of NaOH }(N)\times 56.1}{\text{Weight of alkyd sample }(g)} \tag{3.11}$$

Figure 3.10: Experimental setup during alcoholysis stage

Figure 3.11: Experimental setup during polyestrification stage

3.12 Characterization of LENR50-alkyd resins

3.12.1 Fourier-transform infrared (FTIR) spectroscopy

The chemical composition of alkyd resin was investigated by Perkin Elmer Spectrum 400 FT-IR/ FT-FIR spectrometer with resolution of 4cm^{-1} from 400 to 4000 cm^{-1}.

3.12.2 Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy

Alkyd resin was dissolved in deuterated chloroform, $CDCl_3$ in the presence of tetramethylsilane, TMS. The samples were analysed using JEOL JNM-GSX 270 NMR spectrometer. Deuterium in $CDCl_3$ locks the magnetic field while TMS functioned as the internal standard to lock the signal at 0 ppm.

3.13 Preparation of LENR50-alkyd coatings

3.13.1 Preparation of coating mixture

Alkyd resin was dissolved in styrene which acted as the reactive diluent at ambient temperature. Alkyd-styrene mixture was stirred until homogenous, then TMPTA and mixture of benzophenone and 1-hydroxycyclohexyl phenyl ketone in ratio of 1:1 were added into the mixture. TMPTA was served as crosslinker while benzophenone and 1-hydroxycyclohexyl phenyl ketone were photointiators. The mixture was stirred again until homogeneity was achieved. The composition of mixture of alkyd resin: styrene: TMPTA: benzophenone+1-hydroxycyclohexyl phenyl ketone was fixed in ratio of 50: 35: 10: 5. For LENR50-alkyd, the resins were dried in oven prior preparation of coating mixture to further get rid of the toluene solvent.

3.13.2 Treatment of mild steel panel

Prior to film application, mild steel panels were treated to remove any impurities covered on the surface meanwhile to minimise the effect of substrate during film property test. Oil or strains on the panels were cleaned off using toluene. After rubbing by paper towels, the remaining toluene was wiped off using acetone. Panels were rubbed by paper towels with acetone until the surfaces were toluene-free and dust-free. Finally, they were wiped dry and kept in desiccator prior to use.

3.13.3 Application and curing of coatings

After coating mixtures were mixed to homogeneity and applied on substrate panels using a bar coater, they were immediately irradiated under UV light to cure. The use of different types of panels was depended on the test carried on the coatings. The UV curing system used was an ELC-4001 UV Flood System with UV-A light irradiation (wavelength= 365nm; intensity=125 mW/cm^2) from 400W lamp at (Figure 3.12). The coatings were left for room conditioning before the following tests were carried out on the films. Figure 3.13 shows the diagrammatical flow on the preparation of LENR50-alkyd coating.

Figure 3.12: UV cure system

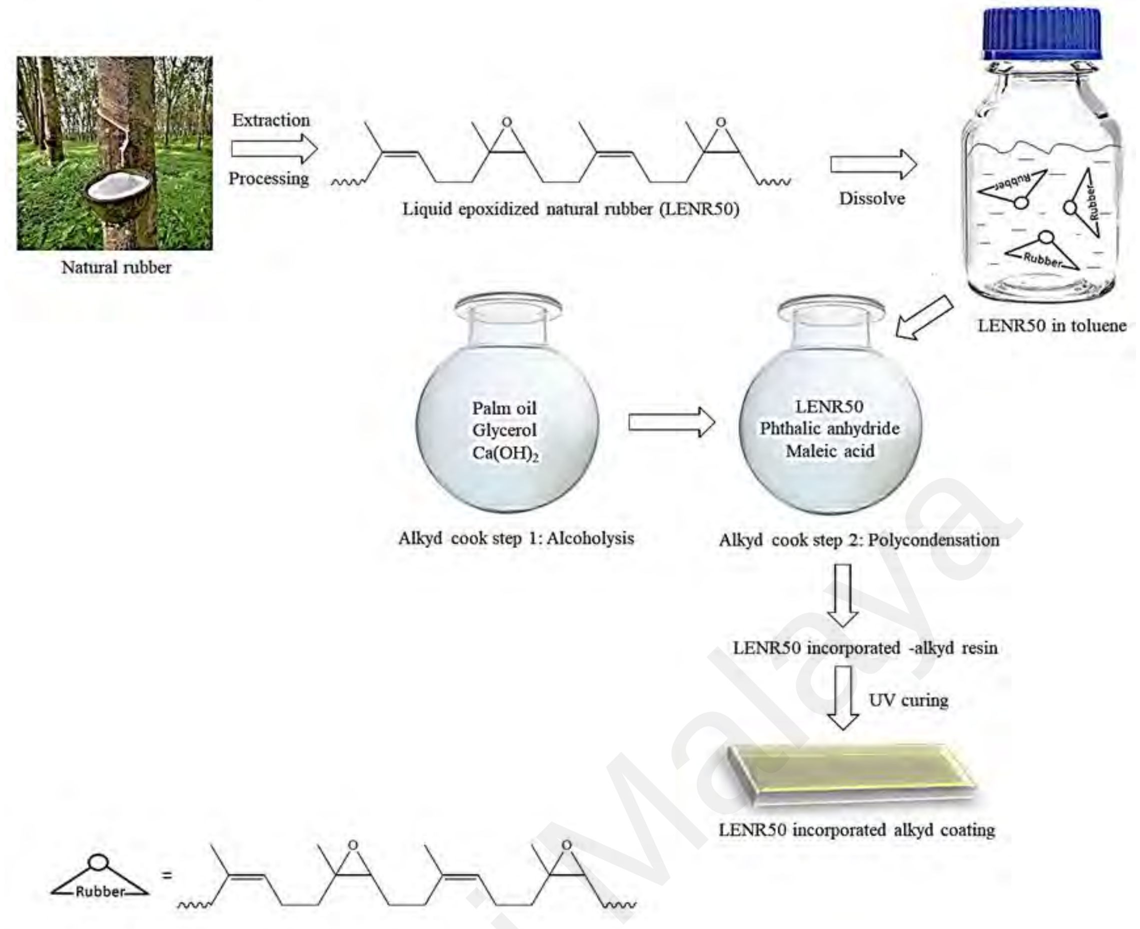


Figure 3.13: Diagrammatical flow on the preparation of LENR50-alkyd coating

3.14 Characterization of UV-cured LENR50-alkyd coatings

3.14.1 Fourier-transform infrared (FTIR) spectroscopy

The chemical composition of cured coating was investigated by Perkin Elmer Spectrum 400 FT-IR/ FT-FIR spectrometer with resolution of 4cm^{-1} from 400 to 4000 cm^{-1}.

3.14.2 Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy

Cured coating was dissolved in deuterated chloroform, $CDCl_3$ in the presence of tetramethylsilane, TMS. The samples were analysed using JEOL JNM-GSX 270 NMR spectrometer. Deuterium in $CDCl_3$ locks the magnetic field while TMS functioned as the internal standard to lock the signal at 0 ppm.

3.15 Determination of film properties of UV-cured LENR50-alkyd coatings

Tests carried out on the coatings are like those carried out in Section 3.6 and Section 3.9, and they include:

(a) Gel content (Section 3.6.1)
(b) Pencil hardness test (Section 3.6.2)
(c) Film adhesion test (Section 3.6.3)
(d) Solvent resistance test (Section 3.6.4)
(e) Water resistance test (Section 3.9.1)
(f) Chemical resistance test (Section 3.9.2)
(g) Contact angle measurement (Section 3.9.3)
(h) Thermal gravimetric analysis (Section 3.6.10)
(i) Differential scanning calorimetry (Section 3.6.11)

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Characterization of UV-ENR25

4.1.1 FTIR spectroscopy

FTIR spectra of ENR25 before UV irradiation, 2 hours UV-ENR25, 4 hours UV-ENR25 and 6 hours UV-ENR25 are shown in Figure 4.1. Absorbance ratios obtained from normalized peak areas were compared for quantitative analysis and the result is shown in Table 4.1. The peak at 871 cm^{-1} is attributed to the epoxide group of rubber and the peak at 838 cm^{-1} refers to unsaturation in rubber. They were normalised with peak at 1451 cm^{-1} that represent the $–CH_2$ bend to account for the potential difference in the film thickness of samples during analysis. Ratio of absorbance of peak at 871 cm^{-1} to 1451 cm^{-1}, A_{871}/A_{1451} of the rubber remained constant at 0.051 and 0.052 for rubber before UV treatment and after irradiated with UV light for 2 and 4 hours, and decreased to 0.040 after 6 hours irradiation. This suggests that the first 4 hours of UV irradiation did not significantly affect the amount of epoxide groups in the rubber but longer period of UV irradiation would cause the deformation of oxirane ring. Based on the absorbance ratio A_{838}/A_{1451}, the amount of unsaturation in rubber has reduced after UV irradiation from 0.137 to 0.071. The trend observed suggests that bulk of the degradation of the rubber has most likely taken place at the C=C of the rubber.

Free radicals are generated during the UV irradiation. The mechanism of UV degradation is presumed to involve radical attack either to the double bond (the main route in UV degradation) or the abstraction of hydrogen atom in the allylic position. UV irradiation generates free radical to attack double bond in rubber chain which resulted in free-radical formation on the chain. By reacting with oxygen, an unstable peroxy radical is formed. Subsequently, an unstable hydroperoxide is formed through the abstraction of a hydrogen atom from another rubber chain. Alkoxy radical is formed by splitting of hydroperoxide group, and then the alkoxy radical continue to propagate the reaction by abstracting another hydrogen. The reaction is terminated by recombination of two radicals or by disproportionation/ hydrogen abstraction. The end products of UV degradation in the presence of oxygen include the chain-scission rubber with peroxide, hydroperoxide, carbonyl and alcohol groups (Rooshenass et al., 2018).

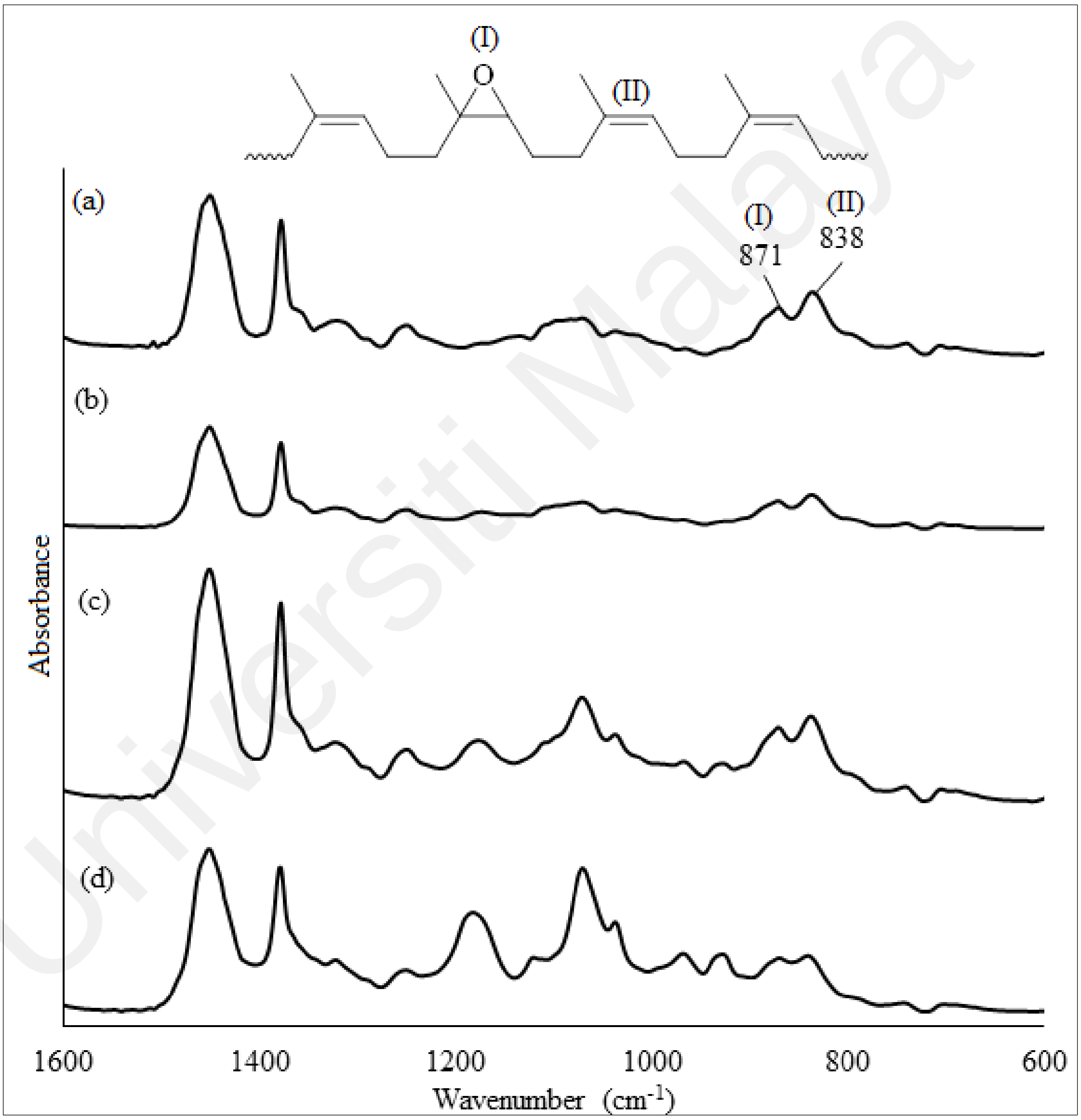


Figure 4.1: FTIR spectra of (a) ENR25, (b) 2 hours UV-ENR25, (c) 4 hours UV-ENR25, and (d) 6 hours UV-ENR25

Table 4.1: Normalized FTIR peak area of unsaturation and epoxide groups in rubber samples

Rubber	FTIR absorbance	
	A_{838}/A_{1451}	A_{871}/A_{1451}
ENR25	0.137	0.052
2 hours UV-ENR25	0.117	0.051
4 hours UV-ENR25	0.073	0.052
6 hours UV-ENR25	0.071	0.040

4.1.2 ^{1}H-NMR spectroscopy

Result from ^{1}H-NMR analysis carried out on rubber samples shows agreement with FTIR. ^{1}H-NMR spectra of rubbers are shown in Figure 4.2. For quantitative analysis, peak area of C=C (5.1 ppm) and epoxide group (2.7 ppm) are normalised using peak at 1.2 ppm which corresponds to $–CH_3$ proton and summarised in Table 4.2. The amount of epoxide group in the rubber remains approximately constant evident from the insignificant difference in normalized peak area, $I_{2.7ppm}/I_{1.2ppm}$ of ENR25 (0.36), 2hr UV-ENR25 (0.35), 4hr UV-ENR25 (0.33), and 6hr UV-ENR25 (0.30). On the contrary, the amount of unsaturation in the rubber showed reduction from $I_{5.1ppm}/I_{1.2ppm} = 0.95$ in ENR25 to 0.60 in 6hr UV-ENR25.

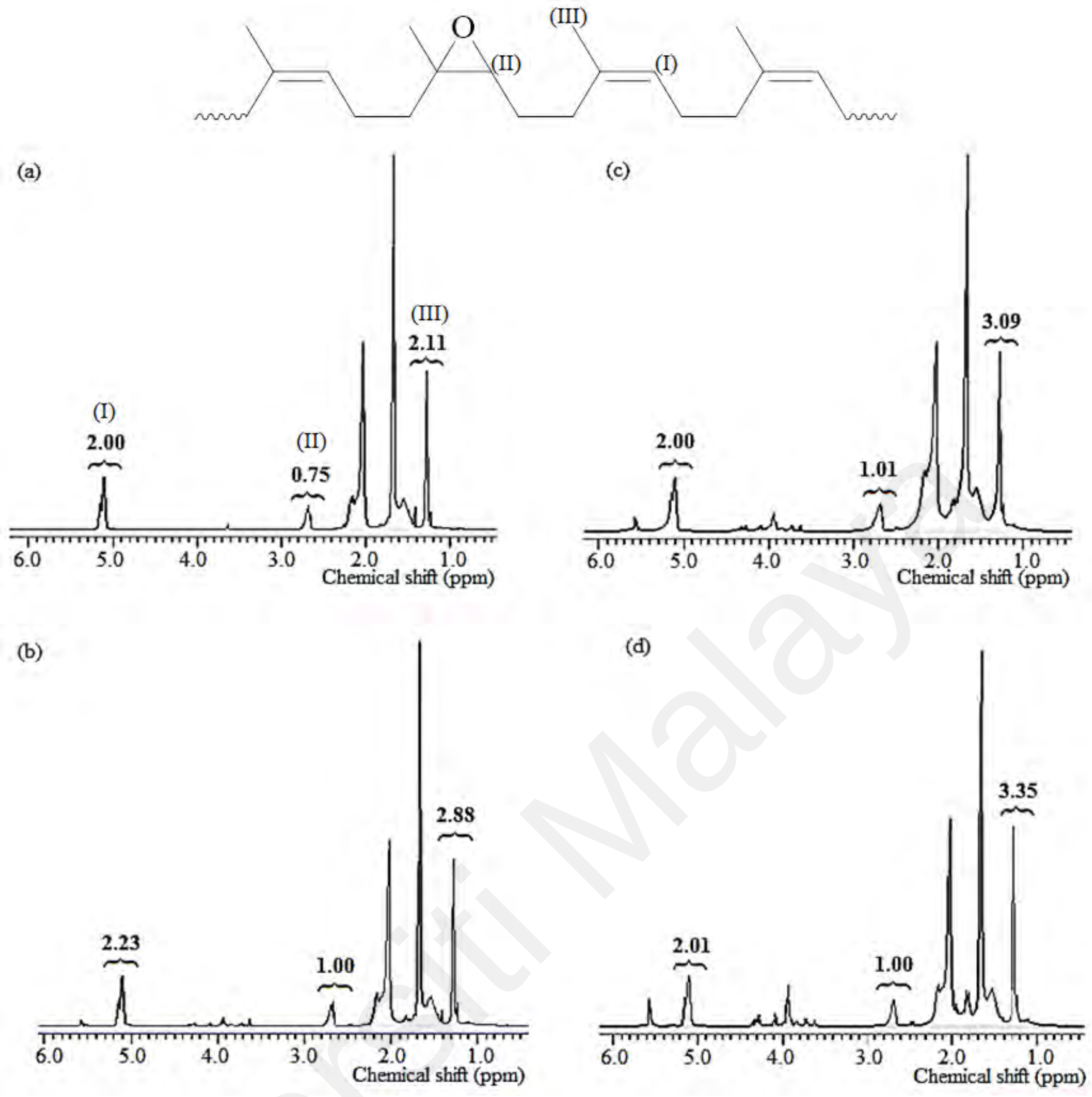


Figure 4.2: ^{1}H-NMR spectra of (a) ENR25, (b) 2 hours UV-ENR25, (c) 4 hours UV-ENR25, and (d) 6 hours UV-ENR25

Table 4.2: Normalized ^{1}H-NMR integral of unsaturation and epoxide groups in rubber samples

Rubber	^{1}H-NMR integral	
	$I_{5.1ppm}/I_{1.2ppm}$	$I_{2.7ppm}/I_{1.2ppm}$
ENR25	0.95	0.36
2 hour UV-ENR25	0.77	0.35
4 hours UV-ENR25	0.65	0.33
6 hours UV-ENR25	0.60	0.30

4.1.3 Gel permeation chromatography

GPC analysis was conducted on ENR25 and UV-ENR25 to study the molecular weight of the rubber as the reduction of molecular weight is decisive for its efficiency to act as an epoxy resin. The number-average molecular weight, M_n and dispersity index of rubber samples are presented in Figure 4.3. The M_n of ENR25 has decreased from 98,484 g/mol before i_t was degraded, to 47,181 g/mol, 22,882 g/mol and 18,101 g/mol after 2 hours, 4 hours and 6 hours of UV treatment, respectively. In addition, the reduction in dispersity index from 3.508 to 1.833 indicates the narrowing of the molecular weight distribution during the UV treatment.

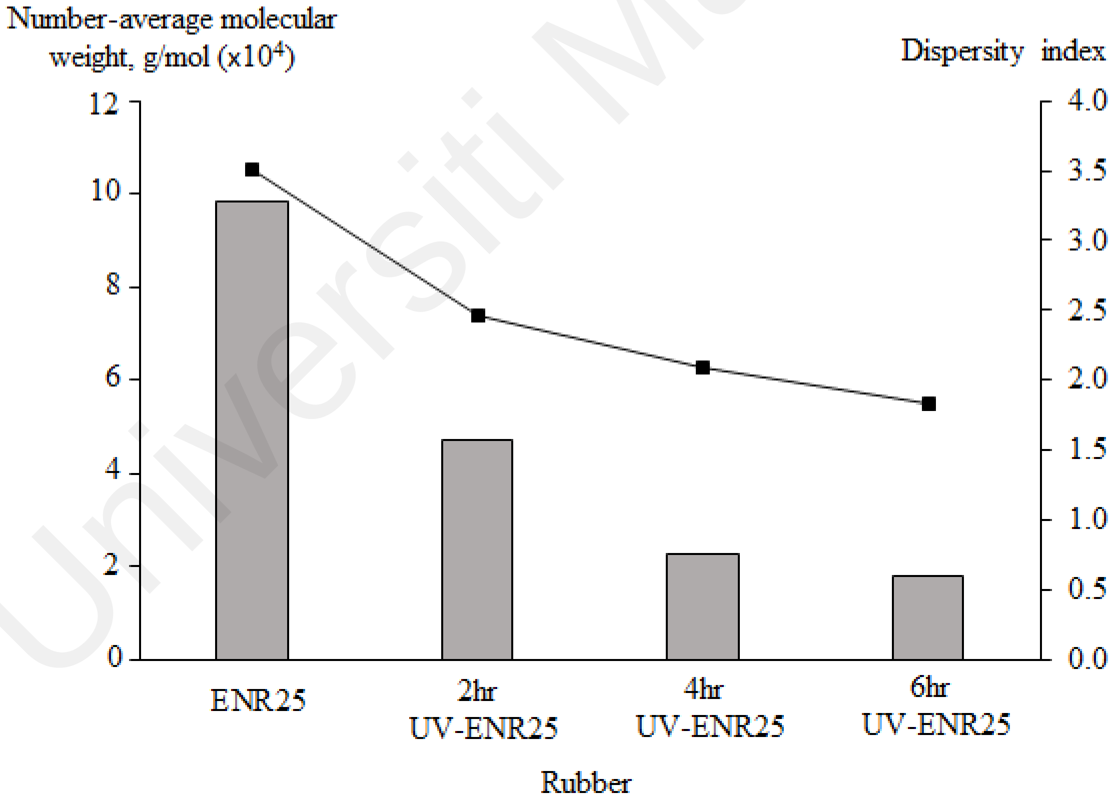


Figure 4.3: Number-average molecular weight and dispersity index of rubber samples

4.1.4 Determination of epoxy equivalent

Preserving the epoxide equivalent value of the rubber throughout the UV treatment is crucial to ensure the availability of the epoxide functional group for further reaction during film formation. The epoxide equivalent value of rubber samples is shown in Figure 4.4. Result reveals there is reduction in epoxide value from 2.953 mol/kg in ENR25 prior to UV degradation to the lowest value at 2.214 mol/kg after UV irradiation. Significant portion of the epoxide groups in the rubber were preserved during the UV irradiation, but conversion of some of the epoxide groups cannot be absolutely avoided considering that the oxirane rings are highly strained and considerably reactive. Majority of the epoxide groups in the rubber remained unreacted and available for further reaction.

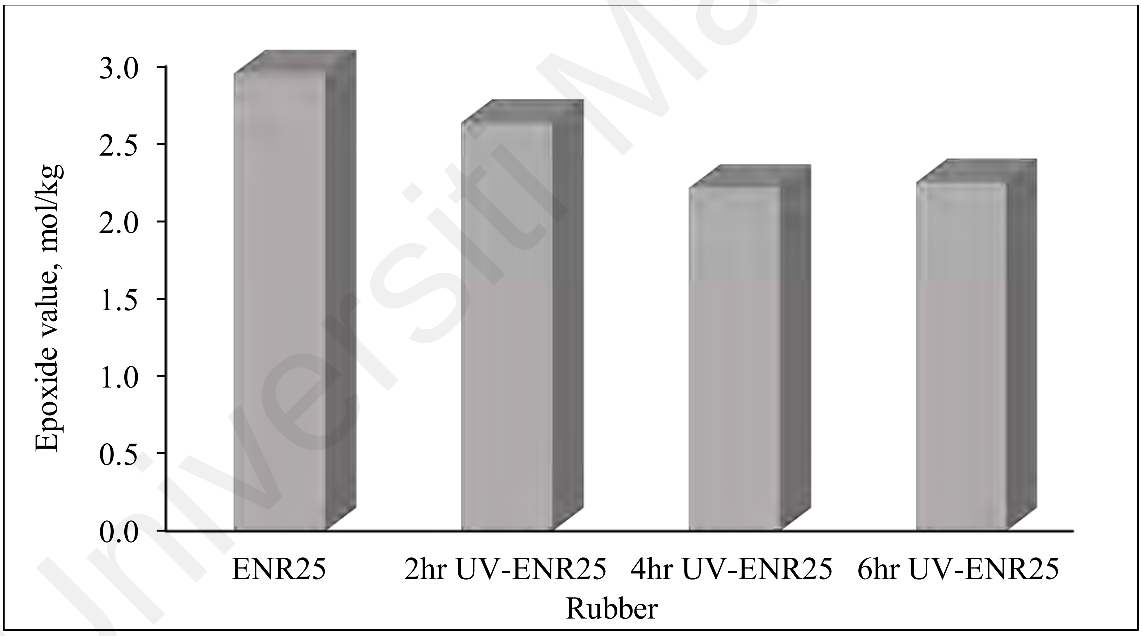


Figure 4.4: Epoxide value of rubber samples

4.2 UV-ENR25/PETMP coatings

4.2.1 Reaction between UV-ENR25 and PETMP

Reaction between UV-ENR25 and PETMP occurred via the reaction between epoxide group of UV-ENR25 with thiol group of PETMP after the two compounds were mixed and heated at temperature 80 ˚C. 6 hours UV-ENR25 was chosen to react in these coating mixtures due to its lowest molecular weight among the three UV-ENR25 and reasonable amount of epoxide groups remained. The proposed reaction is illustrated in Figure 4.5. Occurrence of reaction is supported by the result of FTIR analysis conducted on the wet coating and cured coating, shown in Figure 4.6. The change in FTIR epoxide peak intensity at 872 cm^{-1} was observed. The peak which was clearly visible in wet coating has reduced significantly after the coating was cured. The change in the physical condition of films observed during the preparation of coatings also supported the occurrence of reaction between UV-ENR25 and PETMP. UV-ENR25/PETMP coatings changed from being wet and tacky in the beginning, to hard and smooth films upon curing at elevated temperature, except for coating R100. Coating R100 which comprised solely UV-ENR25 remained relatively soft due to the absence of PETMP, hence extent of crosslinking in the film is minimal, if any.

To highlight the importance of epoxide group in UV-ENR25, a simple control study was conducted using UV-degraded natural rubber without epoxidation, named UV-SMR20 henceforth. UV-SMR20/PETMP coating was prepared under same condition as UV-ENR25/PETMP coatings. UV-ENR25/PETMP coating was able to harden and formed smooth film within 24 hours, however, UV-SMR20/PETMP coating remained tacky even after more than 72 hours of heating. The tackiness of UV-SMR20/PETMP SMR20/PETMP coating suggests that no notable reaction has taken place between UV-

SMR20 and PETMP. This drastic difference observe indicate that the epoxide group in UV-ENR25 is indeed vital for the reaction with PETMP to form hard and tack-free film.

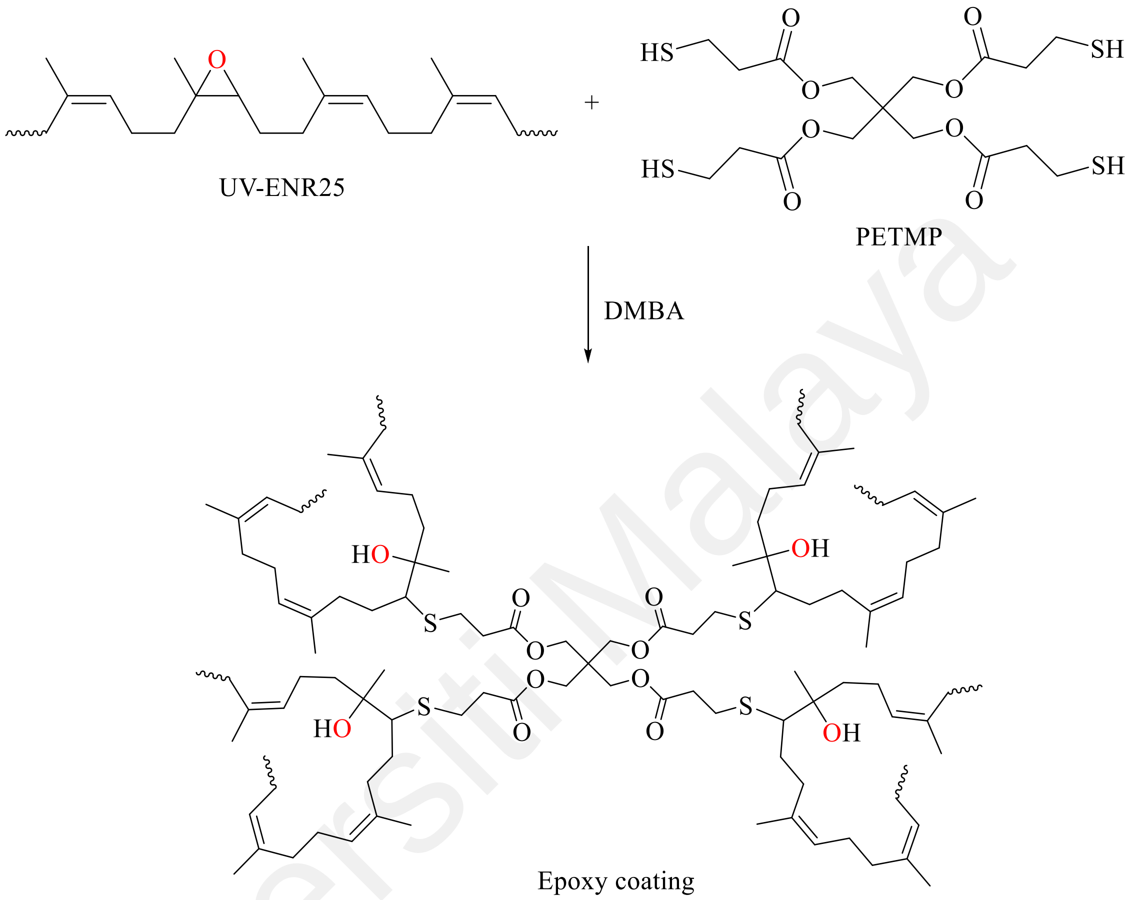


Figure 4.5: Proposed reaction between UV-ENR25 and PETMP

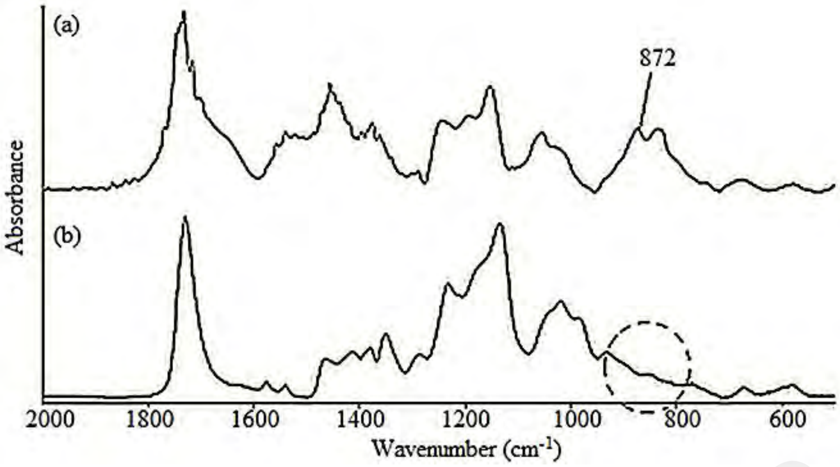


Figure 4.6: FTIR spectra of (a) Wet UV-ENR25/PETMP coating, and (b) Cured UV-ENR25/PETMP coating

4.2.2 Film properties of cured UV-ENR25/PETMP epoxy coatings

(a) Gel content

Gel content was conducted on coatings to study the occurrence and extent of crosslinking between UV-ENR25 and PETMP. The result of gel content is shown in Figure 4.7. In general, highly crosslinked polymer tends to resist total dissolution and retains higher percentage of gel; when the degree of crosslinking is low, the polymer tends to dissolve and leave small amount of gel, if any. Coating R67 and R57 recorded the highest percentage of gel content at 69 % and 66 %, respectively. These two coatings may have the optimal ratio of epoxide: thiol group that facilitate greater amount of crosslinking formed between UV-ENR25 and PETMP. Other coatings recorded relatively lower percentage of gel content could be caused by excess of one of the reactants in the formulation. In consequence, there was more unreacted free components dissolved from the films into the solvent during immersion. Coating R100 recorded the lowest gel content which is < 1 %, and this is because it lacked crosslinking in the absence of hardener and resulted with almost complete dissolution during immersion.

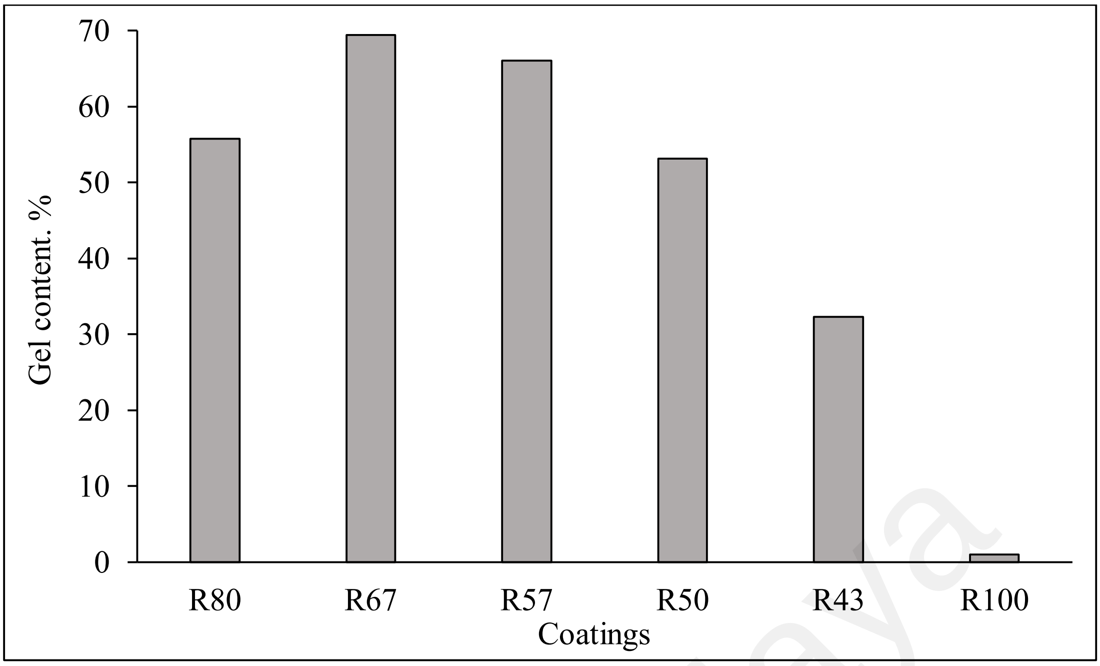


Figure 4.7: Percentage of gel content of UV-ENR25/PETMP coatings

(b) Pencil hardness test

Pencil hardness test was carried out on coatings to test and compare their film hardness. Coating R67 and R57 recorded the highest hardness with pencil grade 4H and 5H, respectively. Coatings R80, R50 and R43 exhibited slightly lower pencil hardness grade, ranging from 2H to 3H. Control coating R100 recorded the lowest film hardness at grade 6B, and this is not unexpected as it was formulated without PETMP which is responsible for crosslinking reaction with the epoxide group of UV-ENR25. The hardness of UV-ENR25/PETMP coatings is comparable with bio-based epoxy coating reported by others. For instance, epoxy coatings cured with bio-based curing agent, cardanol-based reactive polyamide by Balgudea et al. recorded pencil hardness grade in range of 2H and 4H (Balgude et al., 2017), and epoxy coating derived from cardanol-based epoxy resin by Kanehashi et al. are within range of 6B to 2B (Kanehashi et al., 2013).

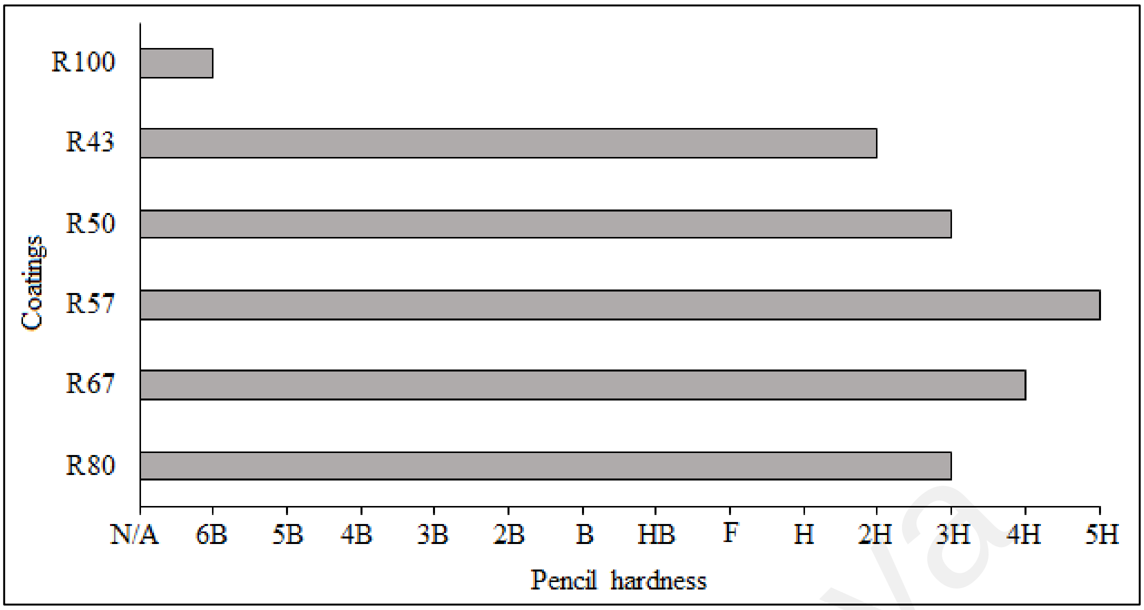


Figure 4.8: Pencil hardness grade of UV-ENR25/PETMP coatings

(c) Film adhesion test

Film adhesive strength of coatings was tested by conducting the cross-cut tape test and the result is shown in Table 4.3. All UV-ENR25/PETMP coatings showed outstanding film adhesion with zero film removal from the mild steel plate. One of the factors could be the interfacial interaction between the coating and substrate. Adhesion can be defined as energy required to separate two adhered materials which involve interfacial bonding of chemical and/or physical bonding. Chemical bonding includes primary valence bond, while physical bonding consists of mechanical interlocking, diffusion, adsorption and electrostatic interaction. UV-ENR25/PETMP coatings comprised of –OH functional groups produced from reaction between epoxide and thiol group, imparted slight polarity to the coatings, thus coatings could form strong interaction with the metal plates. Control coating R100 recorded approximately 5 % of film removal. The film adhesion of coating R100 was better than expected presumably due to the slightly polar epoxide groups as well as due to the strong adhesion promoted by the tackiness of the inner layer of UV-ENR25 that is in contact with the mild steel plate. Property of substrate also influence the strength of adhesion such as its surface energy, contamination, effective surface area and morphology (Ebnesajjad & Landrock, 2014). In this work, the effect from substrate on film adhesion of coatings was made constant by using substrate from same source and treated the same way prior to film applications.

Table 4.3: Percentage of film removal of UV-ENR25/PETMP coatings

Coatings	Film removed, %	Adhesion grade
R80	0.0	5B
R67	0.0	5B
R57	0.0	5B
R50	0.0	5B
R43	0.0	5B
R100	5.0	3B

(d) Solvent resistance test

Solvent resistance of coatings was tested by rubbing the films with MEK solvent in total of 25 full cycles and the result is shown in Figure 4.9. MEK is chosen to carry out the solvent resistance test on coatings because it is a highly effective solvent which is naturally corrosive and able to remove paints and coatings efficiently. Coating R67 to R43 recorded the least film thickness loss, ranging from 0.003 to 0.006 mm. Coating R80 experienced higher film thickness loss, 0.016 mm, and this could be due to the excess amount of UV-ENR25 in the formulation that has resulted with dissolution of the non-crosslinked rubber in the film during the test. Control film, R100 which has the least extent of crosslinking experienced highest film thickness loss which is 0.022 mm.

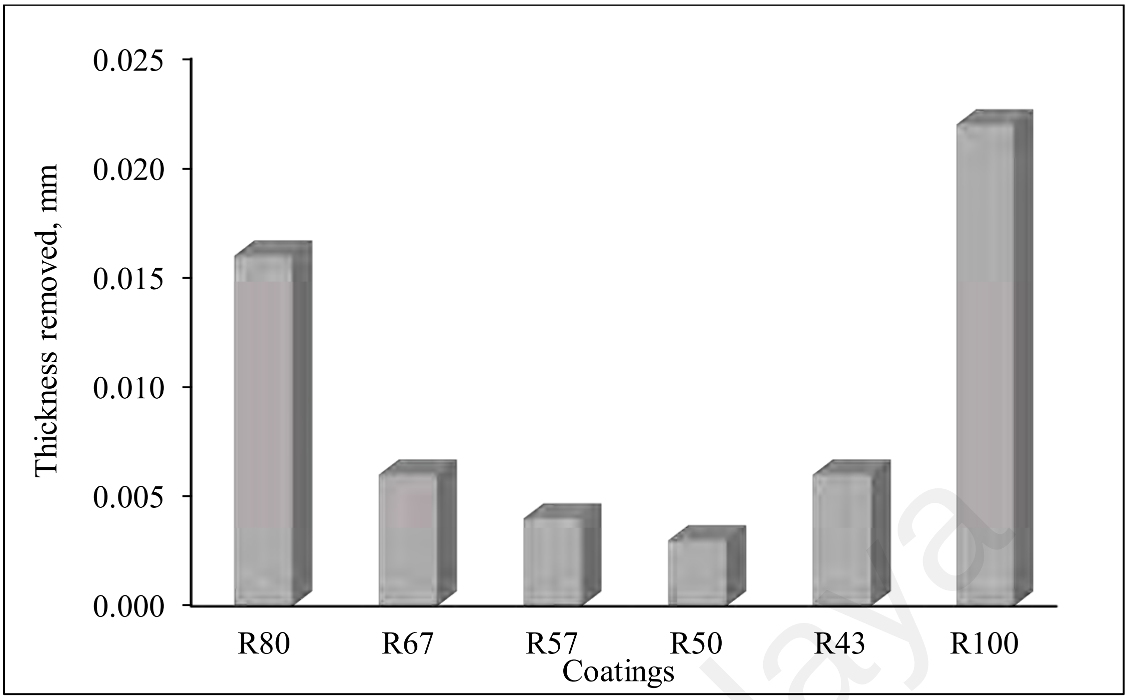


Figure 4.9: Thickness of UV-ENR25/PETMP coating films removed after 25 full cycle rubs with MEK solvent

(e) Water resistance test

Water resistance test was conducted on coatings by immersing them in distilled water for 24 hours at ambient temperature followed by observing the appearance of the coatings. All coatings exhibited slight whitening after immersion, however the whitening disappeared, and the coatings returned to pre-immersion condition in less than 1 hour of conditioning at room temperature. This observation indicates that there was no permanent damage to the films since the changes were reversible within short duration of time.

Table 4.4: Observation on appearance of UV-ENR25/PETMP coatings after immersion in distilled water

Coatings	Water resistance	
	Once removed from water	Room conditioning
R80	Slight whitening	Revert to original appearance < 1 hour
R67	Slight whitening	Revert to original appearance < 1 hour
R57	Slight whitening	Revert to original appearance < 1 hour
R50	Slight whitening	Revert to original appearance < 1 hour
R43	Slight whitening	Revert to original appearance < 1 hour
R100	Slight whitening	Revert to original appearance < 1 hour

(f) Chemical resistance test

Chemical resistance test was carried out by immersing coatings in HCl, NaOH and NaCl solution for 1 hour at 80 ˚C, separately. All coatings remained unaffected from the immersion and they were free from any film depreciation such as blistering, discolouration or film removal.

Table 4.5: Observation on appearance of UV-ENR25/PETMP coatings after immersion in HCl, NaOH and NaCl solution

Coatings	Acid resistance	Alkaline resistance	Saltwater resistance
R80	√	√	√
R67	√	√	√
R57	√	√	√
R50	√	√	√
R43	√	√	√
R100	√	√	√

√ = Film not significantly affected from the immersion test

(g) Water contact angle

Water contact angle test result of the coatings is shown in Figure 4.10. The hydrophobicity of coatings decreased with the introduction of PETMP. The contact angle of coating R100 which comprised of rubber only was at 89.8˚, while the contact angles of UV-ENR25/PETMP coatings decreased to the range of 58˚ – 64˚. The decrease in the contact angle was attributed to the high concentration of polar functional groups in PETMP and also due to the fact that one –OH group is formed for each oxirane ring opening reaction with thiol group. Presence of these polar functional groups caused the coatings to be more hydrophilic than the control.

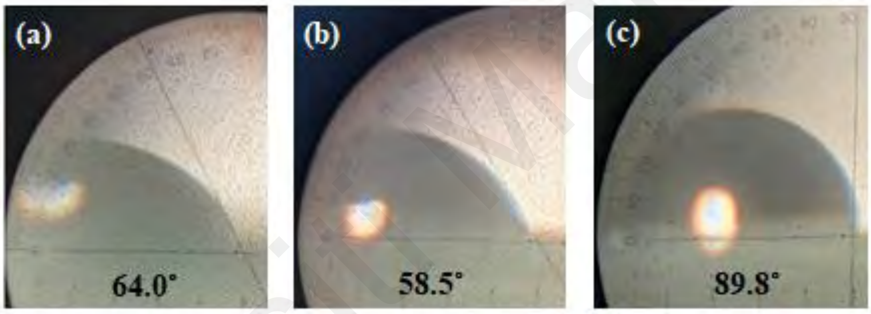


Figure 4.10: Contact angle of coating (a) R80, (b) R50, and (c) R100

(h) TGA thermal analysis

TGA thermal analysis was conducted on the coatings to study their thermal stability, and the thermograms are shown in Figure 4.11. Coating R67 started to undergo degradation at temperature just above 200 ˚C, while the onset of degradation of coating R100 was slightly higher which was close to 250 ˚C. The lower onset of degradation showed in coating R67 is presumably owing to the trace amount of unreacted PETMP that were trapped in the films. From Figure 4.11 (a), there is a notable difference observed at temperature around 500 ˚C, where coating R100 has undergone almost complete weight loss, however, coating R67 still retain significant amount of weight before complete decomposition at 800 ˚C. This could be contributed to the formation of crosslinking through the reaction between UV-ENR25 and PETMP which allow the coating to endure higher temperature prior to degradation. The 1st derivative TGA curve of coatings shown in Figure 4.11 (b) reveals that the peak temperature at which maximum decomposition occurred in coating R100 was about 436 ˚C, whereas those of coating R67 were around 454 ˚C and 725 ˚C.

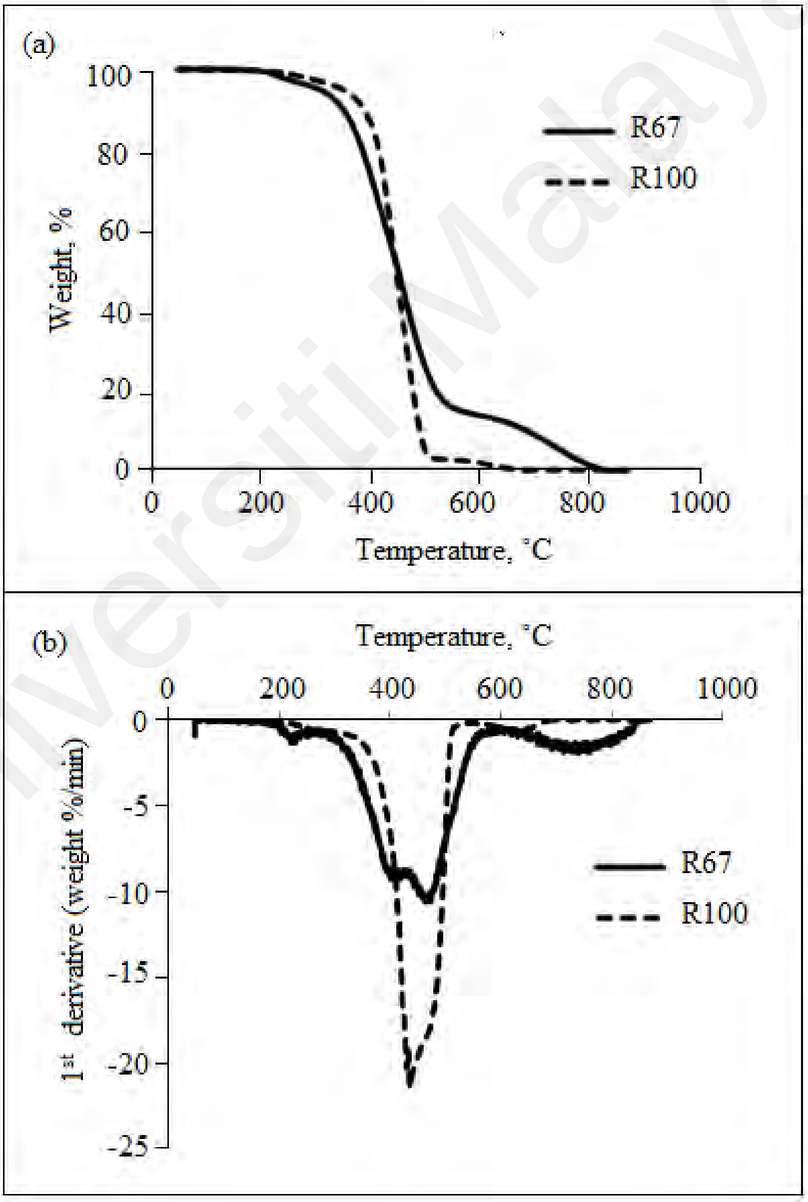


Figure 4.11: (a) TGA thermograms of coatings R67 and R100, (b) 1st derivative TGA thermograms of coatings R67 and R100

(i) DSC thermal analysis

The DSC curves and glass transition temperature, T_g (shown in bracket) of coatings are shown in Figure 4.12. The midpoint of glass transition, T_g of coating R67 at 30.7 ˚C is remarkably higher than the control coating R100. The improvement in T_g is owing to the formation of crosslinked polymer network in the coating via reaction between UV-ENR25 and PETMP, subsequently higher amount of energy was needed for the transition from glassy to rubbery state.

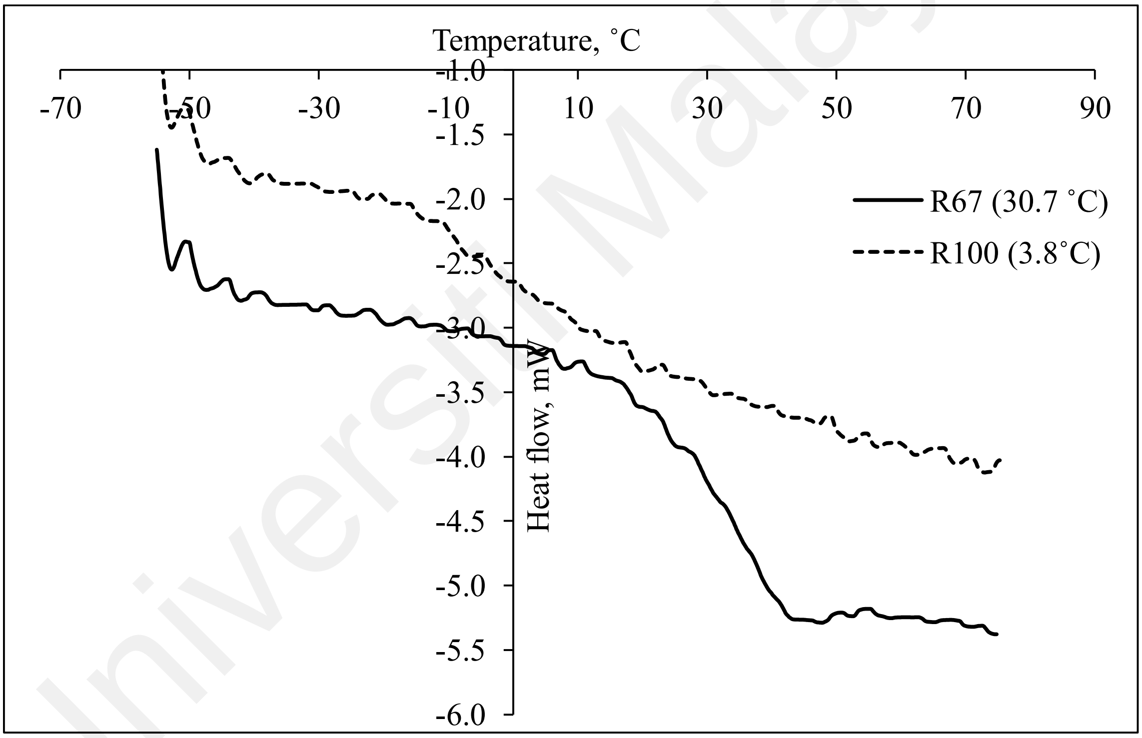


Figure 4.12: DSC thermograms of coatings R67 and R100

4.3 UV-ENR25/Tannic acid coating

4.3.1 Reaction between UV-ENR25 and tannic acid

Proposed reaction between UV-ENR25 and tannic acid is shown in Figure 4.13. The reaction between UV-ENR25 and tannic acid took place through the reaction between epoxide groups of UV-ENR25 with phenolic hydroxyl groups of tannic acid after the two compounds were mixed and heated at 80 ˚C. An ether linkage and a new –OH functional group were generated from reaction between epoxide of rubber and phenolic –OH group of tannic acid. The less hindered –OH groups of tannic acid, especially those located in the outer layer of gallic acid unit are expected to have higher chances to react with oxirane rings of UV-ENR25. The physical condition of coatings turned from tacky films to hard and dry films after curing at elevated temperature. The whole range of coatings experienced this physical transformation except control coating R100 which remained relatively soft and tacky. This is because it contained solely degraded rubber, without tannic acid which is responsible for crosslinking reaction. There was inhomogeneity observed in coating T65 and T80 (Figure 4.14). Increase in the proportion of tannic acid from coating T50 to T80 have resulted with excess of phenolic –OH: epoxide groups, and consequently the interaction between the UV-ENR25 and tannic acid weakened and resulted with inhomogeneity.

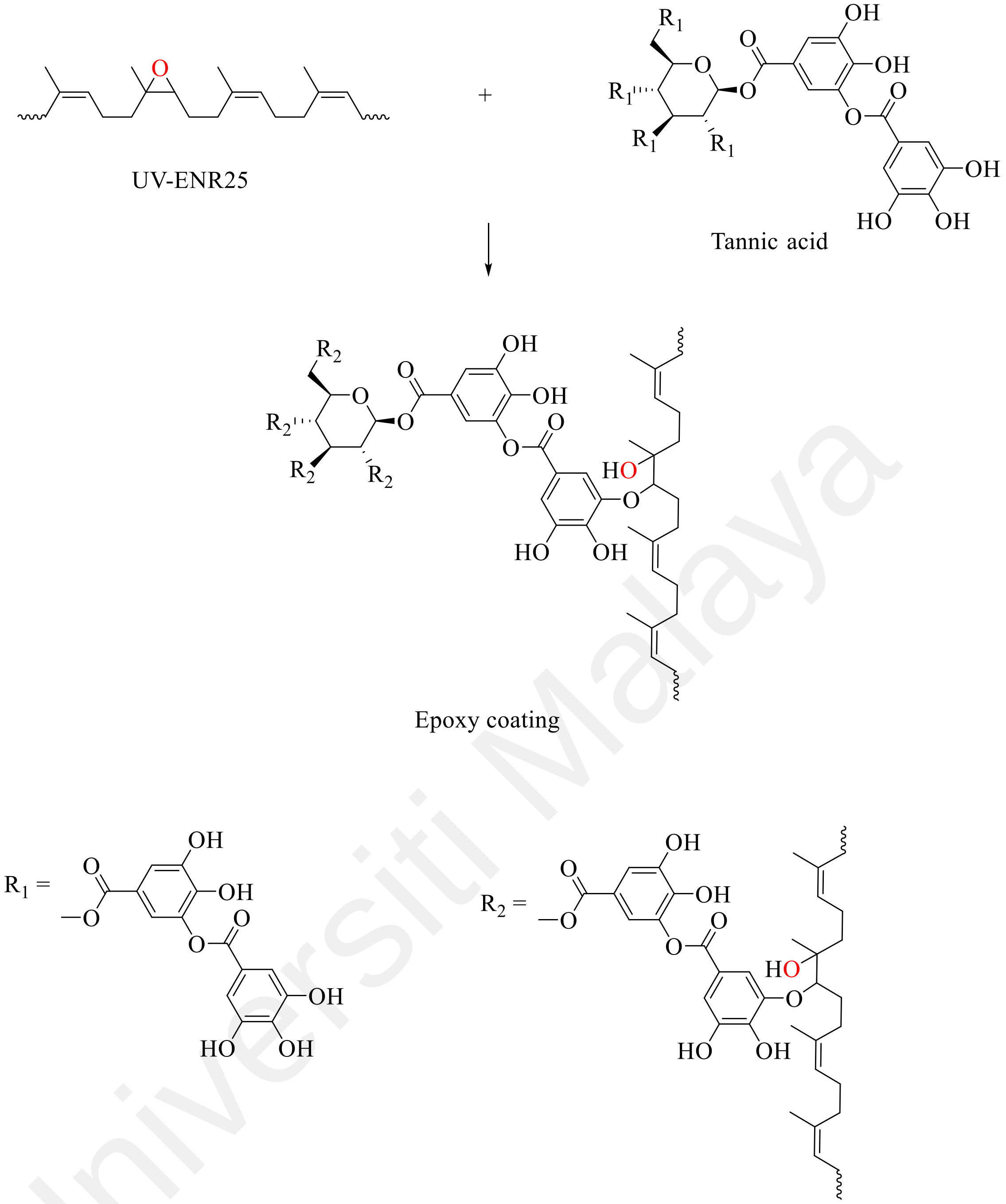


Figure 4.13: Proposed reaction between UV-ENR25 and tannic acid

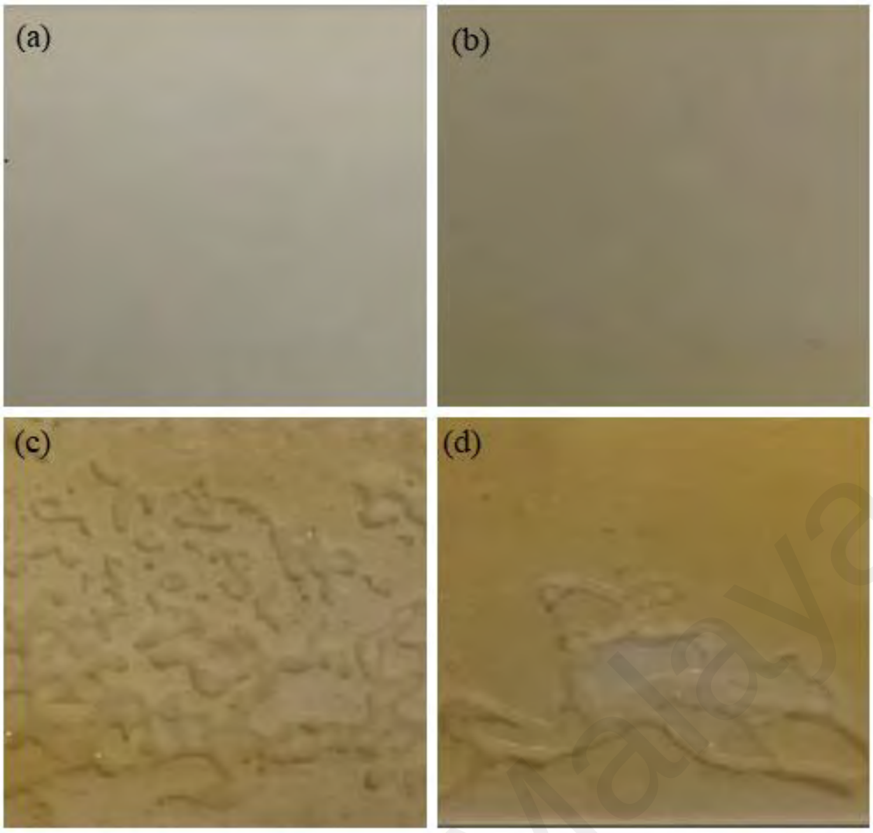


Figure 4.14: Surface condition images of (a) coating T10, (b) coating T20, (c) coating T65 and (d) coating T80

FTIR spectrum of UV-ENR25/tannic acid coating, represented by coating T10 is shown in Figure 4.15. Peak at 3200 cm^{-1} is attributed to –OH stretching, peaks at 2961 cm^{-1}, 2925 cm^{-1}, 2856 cm^{-1} indicate the presence of sp^3 hybridised C-H groups, peak at 1611 cm^{-1} represents C=C stretching while other major peaks at 1705 cm^{-1} and 1085 cm^{-1} are attributed to C=O and C-O groups, respectively.

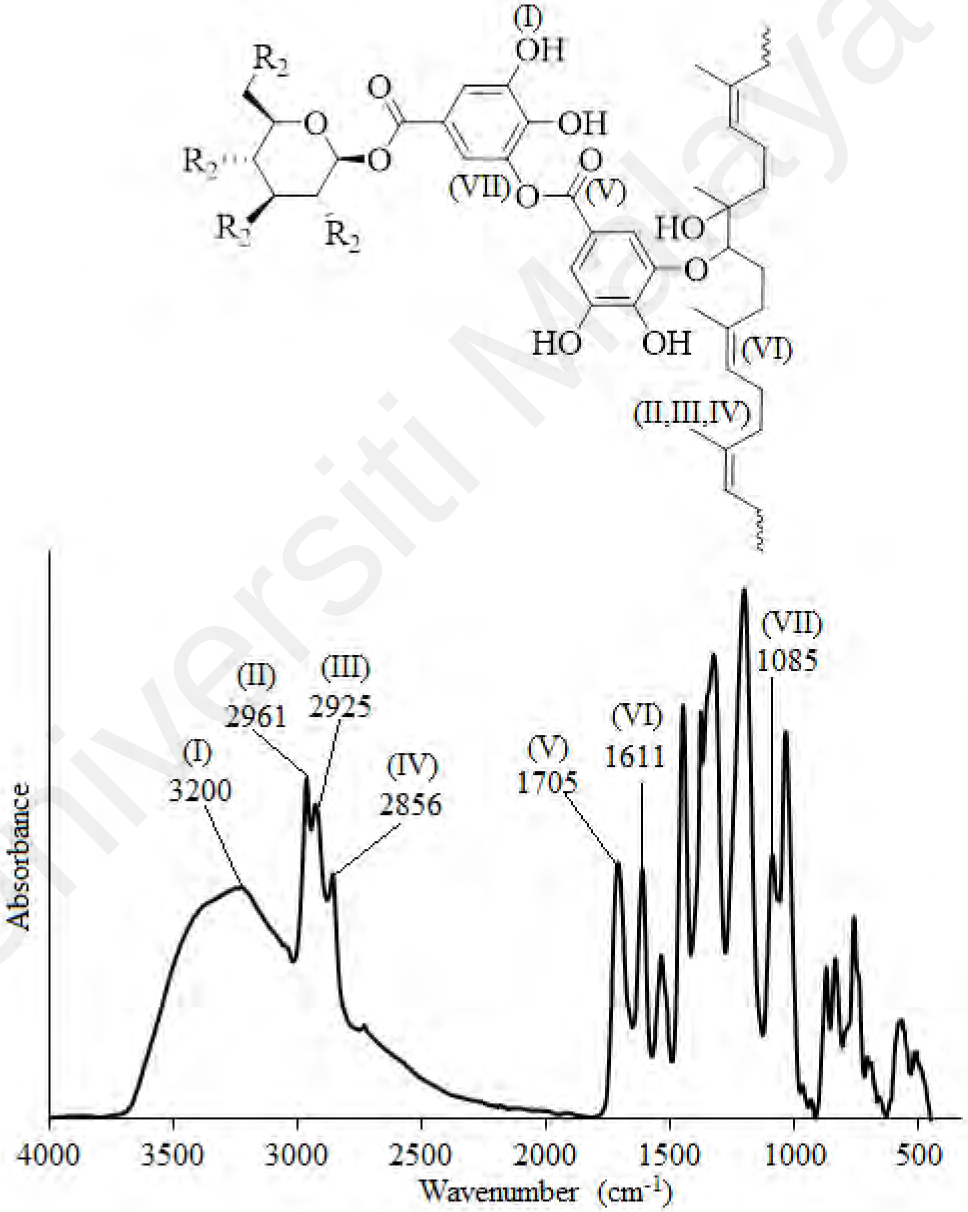


Figure 4.15: FTIR spectrum of coating T10

4.3.2 Film properties of cured UV-ENR25/tannic acid epoxy coatings

(a) Gel content

Result of gel content test carried out on the coatings is shown in Figure 4.16. Coating T10 and T20 recorded the highest gel content at 76.6 % and 71.9 % respectively. The percentage of gel content decreased gradually to below 10 % for coating T80. The increase in the proportion of tannic acid in formulations lead to the decreasing ratio of epoxide: phenolic –OH groups in coatings and this accounted for the reduction in the percentage of gel produced. The gradual increase in proportion of tannic acid resulted in significant excess of –OH groups and this retards the extent of crosslinking in the film. As the amount of tannic acid increased, more unreacted tannic acids dissolved into THF solvent during the immersion. As a result, coating T50, T65 and T80 experienced more significant dissolution in solvent, recording less than 50% of gel content. Considering the film inhomogeneity and the poor gel content results, coatings T50, T65 and T80 were omitted from further tests. The percentage of gel content of UV-ENR25/tannic acid coatings, especially coating T10, T20, T20-X5 and T20-X9 were comparable to that of UV-ENR25/PETMP, coating R67 and R57 which recorded highest gel content close to 70 %. This implies that epoxy coatings produced from reacting with naturally resourced hardener, tannic acid is not necessarily inferior to that formulated with petrochemical-derived hardener.

The percentage of gel produced by coating T20-X5 and T20-X9 after the immersion were not much different than that of coating T20. This is probably due to the addition of small amount of DGEBA provided limited effect and does not translate to any improvement in the gel content of the coatings. Other than that, unreacted DGEBA molecule tends to leach out easily from the films as it is a relatively small molecule, and this could have contributed to lower gel content than initially expected. It is noteworthy that formulations of coating T20-X5 and T20-X9 had same ratio of epoxide: phenolic – OH groups with coating T20 but the formers have additional 5 % and 9 % of DGEBA, respectively. The controls, coating R100 and T100, recorded the lowest percentage of gel content. Since coating R100 and T100 comprised of solely UV-ENR25 or tannic acid, respectively, the absence of the second component in each film had retarded the extent of crosslinking and subsequently leaded to almost complete dissolution of the film during the immersion. The significant difference in the gel content of control films with UV-ENR25/tannic acid films provided evidence to the reaction between the rubber and tannic acid.

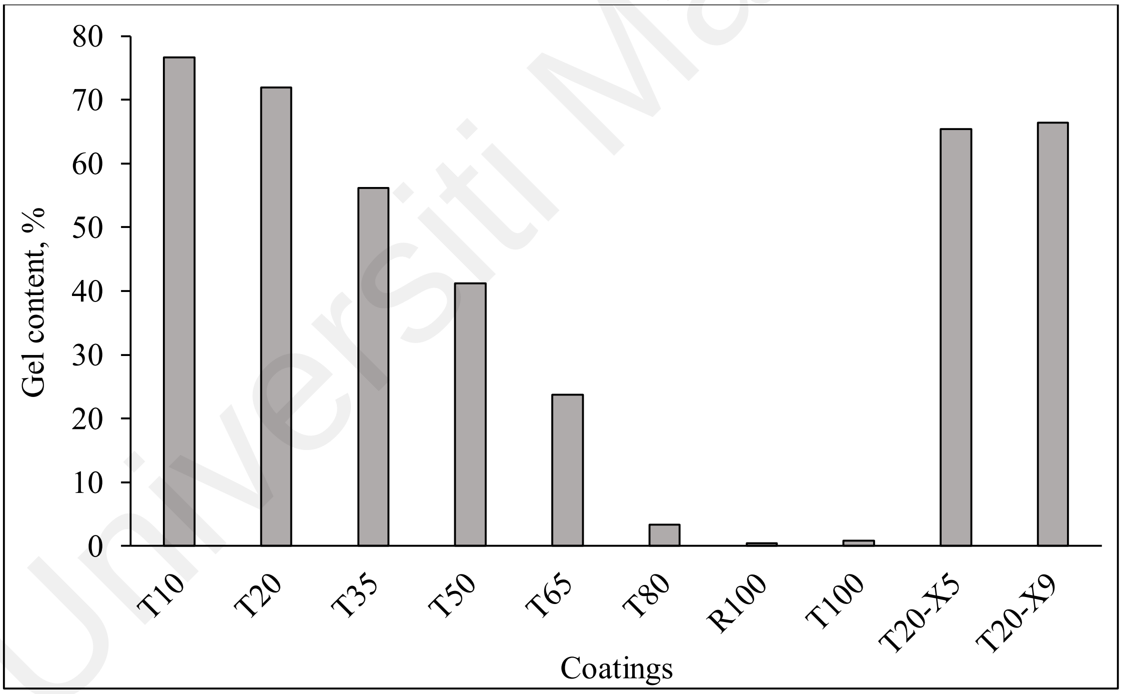


Figure 4.16: Percentage of gel content of UV-EN25/tannic acid coatings

(b) DSC thermal analysis

Thermal behaviour of coatings was studied using DSC, and the results are shown in Figure 4.17. Control coating R100 recorded the lowest T_g at -42 °C, while coating T10, T20 and T35 have relatively higher T_g in the region of approximately -30 °C. The increase in the T_g of the coatings suggest crosslinking between the UV-ENR25 and tannic acid in the coatings has taken place, thus more heat energy was needed for the transition of cured UV-ENR25/tannic acid from glassy state into rubbery state. Coating T20-X5 had experienced even greater increase in T_g which was approximately -25 °C. This is presumably due to the addition of DGEBA in the coating formulation leaded to the increase in the extent of crosslinking in the system. As DGEBA has relatively small molecular size, it probably has greater mobility and able to reach out to some of the more hindered phenolic –OH groups for reaction, and consequently extends the crosslinking in the system. However, the effect from addition of DGEBA is limited, as further addition of DGEBA did not show any apparent improvement in the T_g of the film, with the T_g of coating T20-X9 (not shown) remained very close to that of coating T20-X5.

Coating UV-ENR25/PETMP showed higher T_g compared to that of coating UV-ENR25/tannic acid. This could be attributed to the hygroscopic nature of tannic acid due to presence of abundant –OH groups leading to increase of moisture content in the chains. Consequently, the formation of hydrogen bonds with polymeric chains increases the distance between polymeric chains. Thus, increases the free volume and caused the lowering of T_g compared to coating UV-ENR25/PETMP (Hancock & Zografi, 1994; Reimschuessel, 1978).

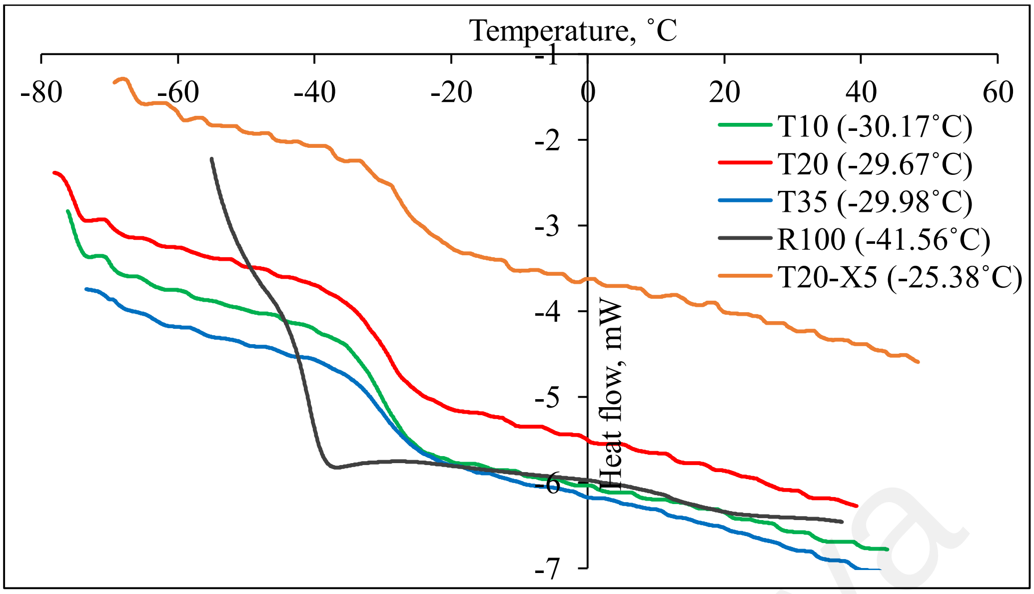


Figure 4.17: DSC thermograms of UV-ENR25/tannic acid coatings

(c) Pencil hardness test

The result of pencil hardness test conducted on coatings is shown in Figure 4.18. For pristine UV-ENR25/tannic acid coatings (coating T10 – T35), coating T20 and T35 recorded highest film hardness with pencil grade HB. Control coating R100 which comprised of solely rubber showed lowest pencil hardness grade at 8B owing to absence of crosslinking in the single component film. Pencil hardness was not carried out on coating T100 because the tannic acid film tends to be brittle when it dried, and easily scratched off from the substrate once the film was in contact with pencil of any hardness grade. Coating T20-X5 and T20-X9 exhibited slight improvement on film hardness from grade HB to F compared to coating T20.

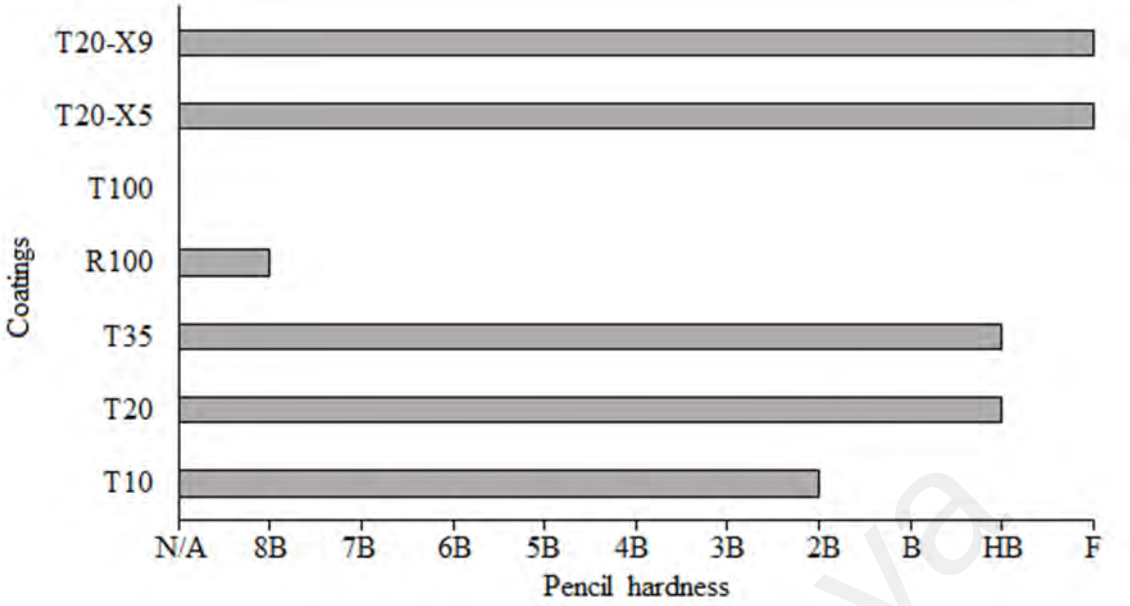


Figure 4.18: Pencil hardness grade of UV-ENR25/tannic acid coatings

(d) Film adhesion test

All UV-ENR25/tannic acid coatings exhibited excellent adhesion on mild steel plates, with all of them recorded close to zero film removal. Coating T20-X5 and T20-X9 with added DGEBA also showed 0% film removal. Other than the –OH functional groups generated from reaction between epoxide and phenolic –OH groups, the presence of abundant –OH functional groups in tannic acid deriver certain degree of polarity to the coating and allows it to form stronger interaction with the mild steel plates. The film adhesion of UV-ENR25/tannic acid coatings is comparable to some of the reported petro-chemical-derived epoxy coatings which recorded adhesion grade at 5B (Alyamac et al., 2012; Meng & Soucek, 2019); and adhesion grade in range of 2B-5B by Rau et al. (Rau et al., 2012).

Table 4.6: Percentage of film removal of UV-ENR25/tannic acid coatings

Coatings	Film removed, %	Adhesion grade
T10	0	5B
T20	1	4B
T35	0	5B
R100	88	0B
T100	-	-
T20-X5	0	5B
T20-X9	0	5B

(e) Solvent resistance test

Result of solvent resistance test is shown in Figure 4.19. Coating R100 recorded greatest film thickness loss at 0.034 mm. The is because the rubber particles in coating R100 were not crosslinked with tannic acid, and the film was readily dissolved by MEK during the test. The other control, coating T100 recorded significantly low film thickness loss, about 0.004 mm. This probably due to the abundance of –OH groups that favour the formation of hydrogen bonding among tannic acid molecules, and thus considerably reduced its solubility in MEK. The UV-ENR25/tannic acid coatings also experienced minimal reduction in the film thickness, ranging from 0.002 to 0.006 mm. The insignificant reduction in film thickness during MEK rub proposes that the cured coatings have relatively good solvent resistance and do not readily dissolve in organic solvent.

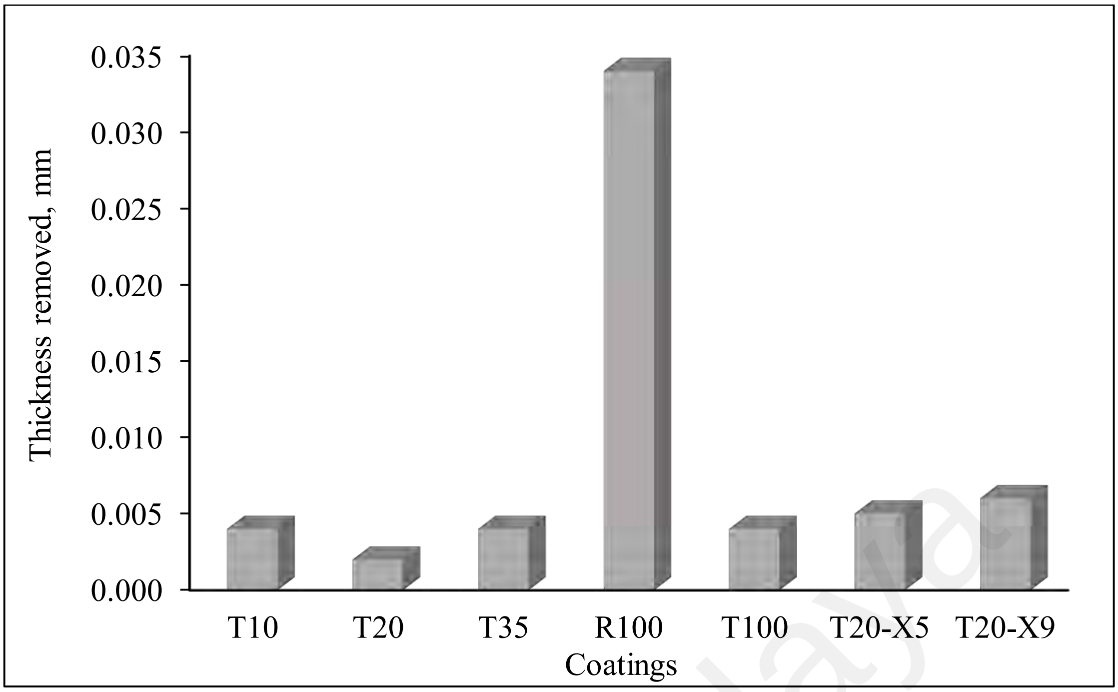


Figure 4.19: Thickness of UV-ENR25/tannic acid coating films removed after 25 full cycle rubs with MEK solvent

(f) Water resistance test

The appearance of the coatings after water immersion is reported in Table 4.7. Coating T100 experienced complete dissolution in water during the immersion, while the rest of the coatings showed satisfactory water resistance owing to the crosslinking between UV-ENR25 and tannic acid. These coatings exhibited slight whitening after 24 hours of immersion, but the whitening disappeared, and the conditions of coatings reverted to their original appearances within 2 hours of drying in room condition. There was no permanent damage such as blistering, or film removal observed. The reasonably good water resistance observed is probably due to the hydrophobic nature of the coating, especially coating T10 and T20 which comprised of high rubber proportion.

Table 4.7: Observation on appearance of UV-ENR25/tannic acid coatings after immersion in distilled water

Coatings	Water resistance	
	Once removed from water	Room conditioning
T10	Slight whitening	Revert to original appearance within 2h
T20	Slight whitening	Revert to original appearance within 2h
T35	Slight whitening	Revert to original appearance within 2h
R100	Slight whitening	Revert to original appearance within 2h
T100	Slight whitening	Complete dissolution
T20-X5	Slight whitening	Revert to original appearance within 2h
T20-X9	Slight whitening	Revert to original appearance within 2h

(g) Chemical resistance test

Chemical resistance test was conducted on the coatings by immersing them in various media (HCl, NaOH and NaCl solutions) for up to 7 days, and the percentage weight change of coatings is shown in Figure 4.20. Coating T100 experienced almost complete dissolution in all the three media. Absent of crosslinking coupled with highly polar composition of the tannic acid film could account for complete dissolution in the aqueous solution. The rest of the coatings, especially coating T10, T20 and T20-X5 exhibited reasonably good chemical resistance with minimal percentage weight change after 1 week of immersion. Most of the tests resulted with weight loss after the immersion due to dissolution of the unreacted components in the films into the solvents, whereas some recorded minimal weight gain, could be owing to the trapped moisture in some of these films.

Qualitative inspection on the condition of coatings after the immersion period was also carried out to evaluate and compare the chemical resistance of the films in the media. No permanent physical damage such as blistering, cracking or tackiness was observed in the coatings after immersion in the HCl and NaCl solutions. Although the films experienced whitening during the immersion, most of them returned to pre-immersion condition after room conditioning for short period of time. The reversible whitening indicates that no permanent damage has taken place. Coating R100 on the other hand, showed persistent film whitening after HCl immersion and did not disappear even after drying for 24 hours. The permanent damage observed in coating R100 could be due to the ring opening reaction of some of the epoxide groups of the rubber by HCl to form halohydrin or diol (Clayden et al., 2012; Solomons & Fryhle, 2011). For alkaline resistance test, other than coating R100, all the films experienced permanent damage in the form of discolouration which is consistent with the relatively high percentage weight change of the coatings after NaOH immersion. The films turned yellow, and the discolouration was irreversible after removing them from medium and drying in oven. The relatively poor performance of UVENR25/tannic acid coatings in alkaline solution could be caused by the reaction between NaOH with some of the unreacted phenolic as well as the presence of ester groups in the films.

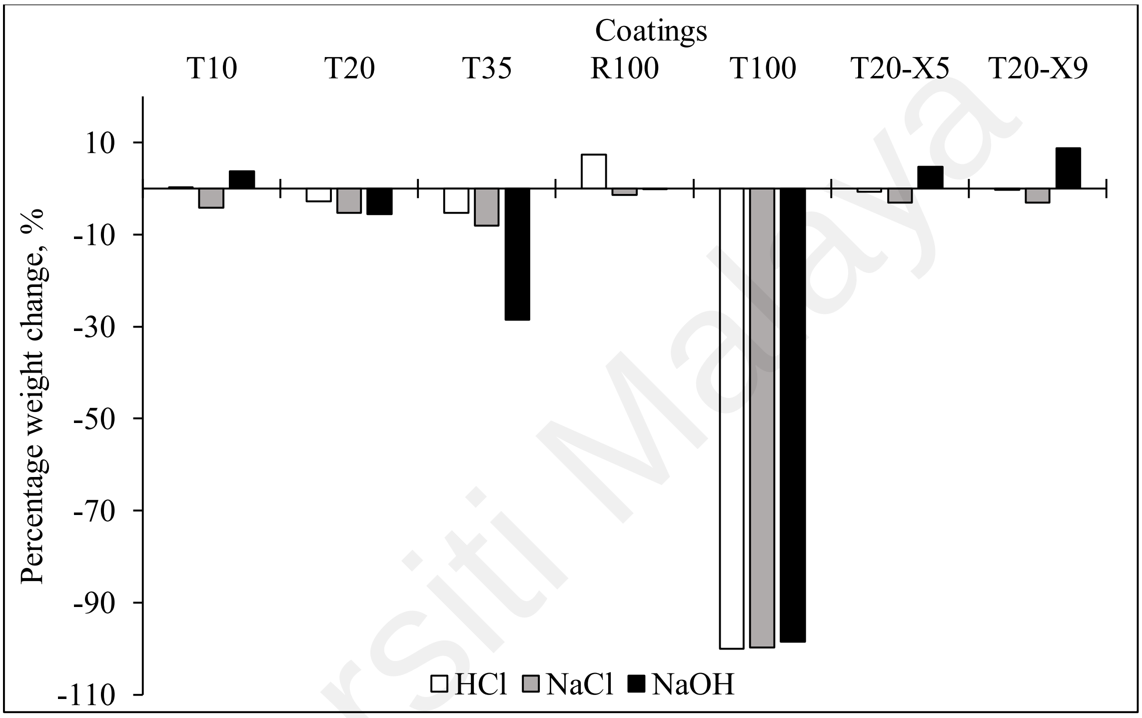


Figure 4.20: Percentage weight change of UV-ENR25/tannic acid coatings after immersion in HCl, NaOH and NaCl

(h) Water contact angle

Water contact angle of the coatings is shown in Figure 4.21. All the coatings recorded contact angles in the range of 92˚ - 96˚, indicating they had hydrophobic surfaces. As UV-ENR25 composes of largely hydrocarbon with small percentage of oxygen, it is unsurprising that these coatings are hydrophobic in nature. Hydrophobic film could be desirable in surface coating application since it has relatively weaker affinity towards water and able to provide better corrosion resistance protection to the metal substrate.

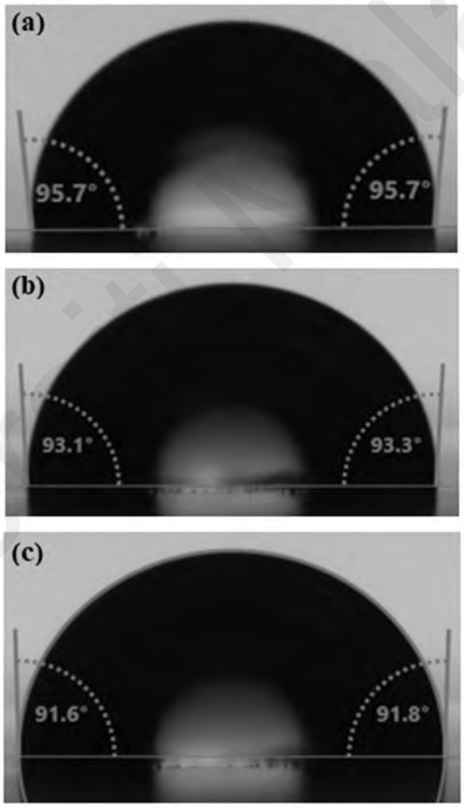


Figure 4.21: Contact angle of coating (a) R100, (b) T20, and (c) T20-X5

(i) TGA thermal analysis

Thermal analysis using TGA was conducted on the coatings, and the results are shown in Figure 4.22. All coatings started to show apparent weight loss at temperature above 300 ˚C, which is considered satisfactory for general application of surface coating. There was minimal weight loss observed prior to that, around 100 ˚C could be from the evaporation of traces of trapped moisture. According to the first derivative curve in Figure 4.22 (b), maximum decomposition of the coatings took place at much higher temperature, above 450 ˚C. This suggests that the coatings have reasonably good thermal stability since such high temperature is needed to break the bulk of the bonds before occurrence of rapid weight loss. By comparing the TGA result of coating T20-X5 with the corresponding coating formulation, coating T20, the former recorded slight improvement in thermal stability. Coating T20-X5 has slightly higher onset of degradation, T_{onset} and higher peak degradation temperature, T_p than coating T20. T_{onset} of coating T20-X5 is 290 ˚C, and T_p is 504 ˚C, while those of coating T20 are 280 °C and 459 ˚C, respectively. The slight improvement observed could be attributed to the inclusion of smaller molecules, DGEBA in the coating formulation that resulted in increase of extent of crosslinking in the system by reaching out to the more hindered –OH group.

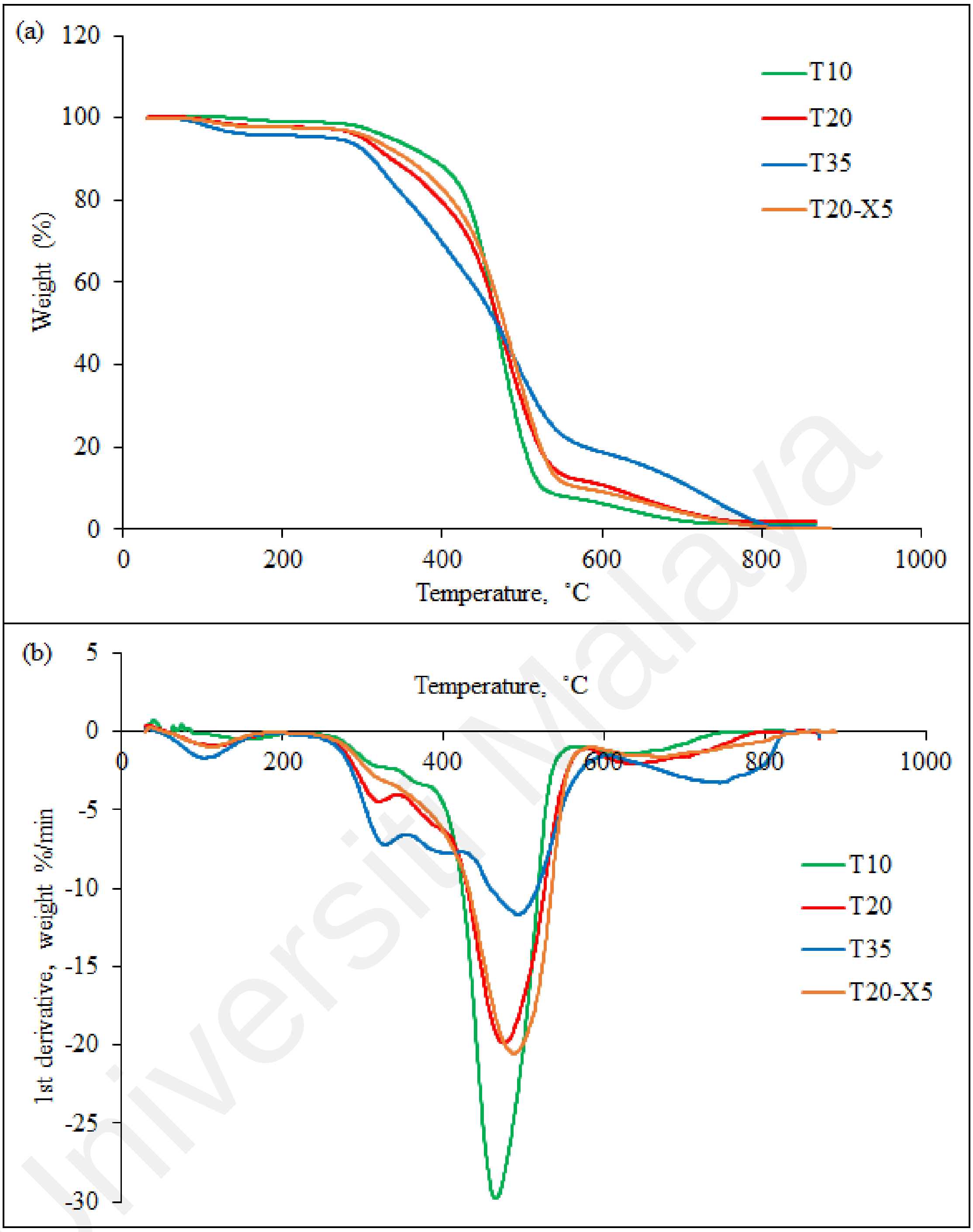


Figure 4.22: (a) TGA thermograms of UV-ENR25/Tannic acid coatings, (b) 1st derivative TGA thermograms of coatings

(j) Biodegradability test

Biodegradability test was conducted on coatings using soil-compost burial method. The percentage of weight loss of coatings after burial is shown in Figure 4.23. The biodegradability test was carried out on UV-ENR25/Tannic acid coatings after considering the high proportion of natural ingredients used in the preparation of the coatings. It is known that microbial degradation of a film starts with adherent of microorganisms on its surface. The presence of polar functional groups such as –OH and ester groups in coating may facilitate this process since the adhesion of bacteria is affected by surface hydrophilicity of samples (Artham & Doble, 2008). Next, surface degradation of sample begins to occur after extracellular enzymes such as depolymerases were secreted from the microbes. Microorganism colony grew throughout the degradation process, and this eventually changes some of the physical as well as chemical properties of the sample (Luyt & Malik, 2019). Some of the notable changes during the degradation process is crazing and discolouration of the sample surface (Geeti & Niranjan, 2019). As the inner region of the samples were exposed due to the surface cracking, further degradation is facilitated. Given enough time, the coatings may be broken down into oligomers and monomers presumably through hydrolysis of ester groups (Geeti & Niranjan, 2019) and oxidative cleavage of C=C double bonds in the polymer chains (Yikmis & Steinbuchel, 2012). Tsuchii et al. have reported biodegradation of natural rubber latex by *Xanthomonas* sp. *strain 35Y* and vulcanized natural rubber by *Nocardia* sp. *Strain 835A* that took place through oxidative cleavage at the C=C of the rubber. After the coating is broken down into smaller fraction, the fragmented products can be ingested by microorganisms, followed by assimilation to produce CO_2, H_2O and microbial biomass. Abiotic biodegradation could happen in parallel or before biotic biodegradation step (Artham & Doble, 2008). Considering the conversion of polymer into gaseous products during biodegradation process, weight loss of samples can be used as an indication of biodegradation. The extent of biodegradability of coatings in this work was evaluated by measuring their percentage weight loss after 12 weeks of soil burial period.

Result of the biodegradation test carried out in the controlled environment in laboratory is shown in Figure 4.23 (a), while the result from the open environment, an outdoor empty grass field is shown in Figure 4.23 (b). Commercially available epoxy coating, henceforth named as coating Epo was included in the test to serve as control, in order to elucidate the difference in the biodegradability between epoxy coatings derived from renewable resources and that of petroleum derivative. Coating Epo experienced < 6% weight loss in both indoor and outdoor soil after 12 weeks period, whereas UV-ENR25/tannic acid coatings recorded up to 62% of weight loss in the test. Deriving materials from renewable resources such as natural rubber and tannic acid have the upper benefit in biodegradation process because plenty of soil microflora are able to digest these natural resources, subsequently results with reasonably good biodegradability of the coatings.

Although UV-ENR25/tannic acid coatings consistently showed higher percentage of weight loss than the control, there is significant difference observed in the extent of weight loss between those of outdoor and indoor sets. The percentage weight loss of coatings buried in soil-compost mixture which kept in laboratory is in overall greater than those buried in empty grass field. For instance, coating T10 from the indoor set recorded the highest weight loss at 62% after 12 weeks, while for outdoor set, coating T35 experienced highest weight loss of 30%. The considerably percentage of weight loss for outdoor set could be due to the warm climate and highly moisture atmosphere during the burial period (meteorological data is provided in section 3.9.4). Since the elevated temperature and humidity levels have been shown to increase the biodegradation of ester-based polymers through increased water absorption and hydrolysis of ester linkages subsequently breaking down the long polymer chains (Copinet et al., 2004). However, the temperature of indoor should be more constant especially at night compared to outdoor. Other than the factor of temperature, this difference could be the consequence of the different fertility of the media used to bury coatings in the two sets of experiments. The soil-compost mixture used for the indoor set has supposedly more nutrients and bacteria strains than that in the soil of empty grass field. The former composed of base fertiliser, various micronutrients and organic matters, making it a highly fertile medium for bacteria growth.

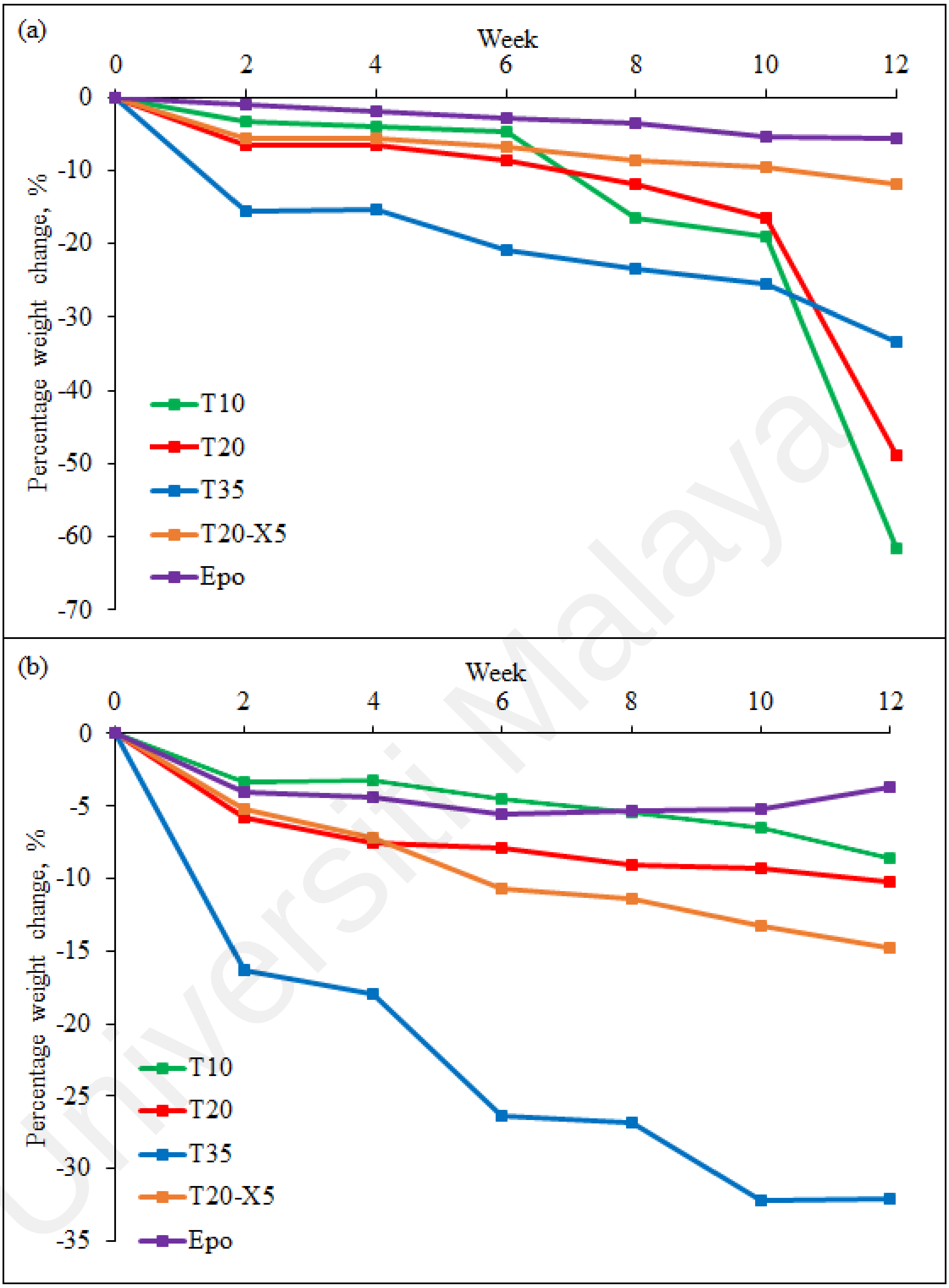


Figure 4.23: Weight % change of UV-ENR25/tannic acid coatings (a) after burial in soil (in lab), (b) after burial in soil (open environment) for 3 months

Changes in the appearance of the coatings throughout the 12 weeks period were inspected and it could indicate the biological activities on the coatings as well. Photographs of some of the coatings throughout the biodegradation process are shown in Figure 4.24. The changes in the appearance of the coatings shows good agreement with the percentage weight loss reported. For indoor biodegradation test, most of the UV-ENR25/tannic acid coatings experienced discolouration and changes in physical appearance. Some of the visual changes are coating films turning reddish-brown, formation of greenish spots that gradually gets bigger on the coating surface, and eventually, disintegration of the coatings. As for outdoor set, coatings showed comparatively similar changes, albeit at slower pace and less intense. Most of them turned brownish, but films remained intact at the end of the test. This agrees with the trend of weight loss recorded, suggesting outdoor biodegradation was taken place at a lower rate compared to those buried in soil-compost medium in indoor setup. Longer time may be needed for the outdoor coatings to attain similar degree of biodegradation as those from indoor set. There is no apparent change observed in coating Epo from the beginning until the end of the test for both indoor and outdoor (not shown) setups. This petroleum-based film remained the same throughout the test, reflecting the poor biodegradability of the films.

Biodegradable coatings are important to protect the substrates at the same time they are able to decompose at reasonably rate after disposing. Since the packaging waste has become a global environmental problem, biodegradable coatings are desirable as they can be broken down easier and cause less harm to the environment. For instance, the paperboard which is widely used as packaging material is normally coated with hydrophobic coating to improve its water barrier property (Han et al., 2010), the biodegradability of coating affect the efficiency of degradation of the packaging materials. Other than packaging, biodegradable coatings are useful in coatings for application of controlled fertilizer release (Lubkowski, 2014), drug delivery (Prabhu & Hossainy, 2007), and monuments and buildings (Ocak et al., 2009) since they are reversible, degradable, and allow new treatment of the material to be protected.

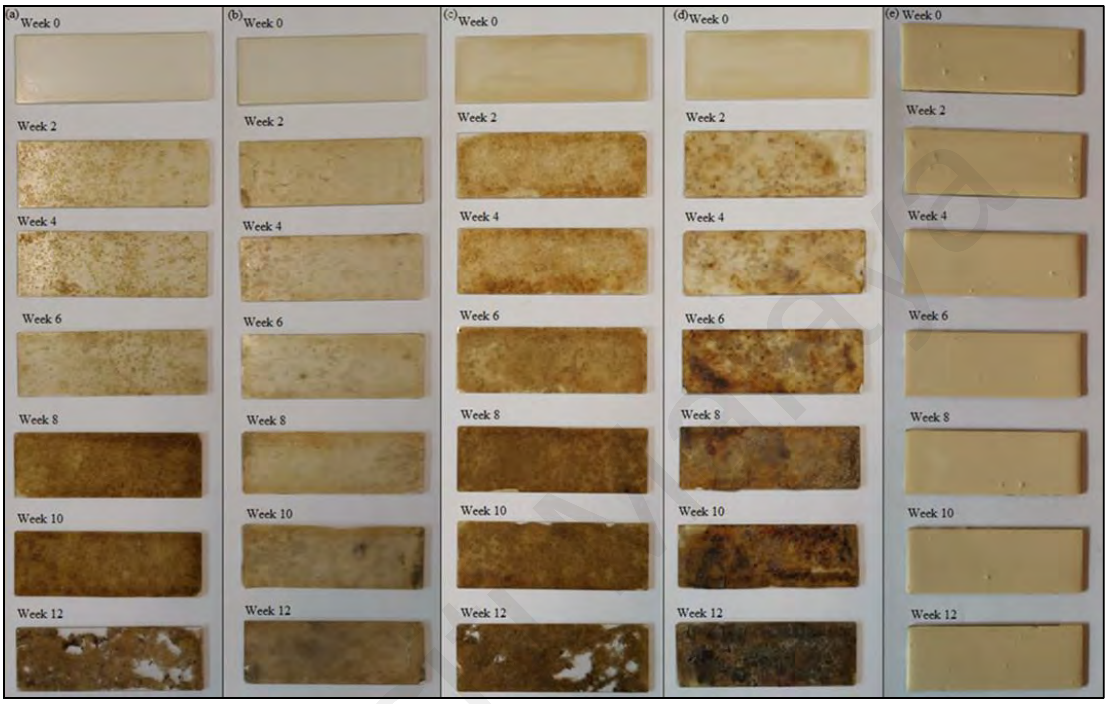


Figure 4.24: Photographs of (a) Coating T10 (in lab), (b) Coating T10 (open environment), (c) Coating T35 (in lab), (d) Coating T35 (open environment) and (e) Coating Epo (in lab) from week 0 to week 12 throughout biodegradation process

4.4 Alkyd coating derived using liquid epoxidized natural rubber

4.4.1 Alkyd synthesis

The proposed reaction in producing LENR50-incorporated alkyd resin is shown in Figure 4.25. The first step was alcoholysis reaction between glycerol and palm oil to yield a mixture of predominant monoglycerides. LENR50 was introduced together with PA and/or MA in the second step. Hydroxyl groups of monoglycerides reacted with anhydride and carboxyl groups of PA and MA to form ester linkages. At elevated temperature, the -COOH groups from the diacids could ring-open the epoxide group of the rubber to form ester group and a new hydroxyl group. Such reaction facilitates the integration of the rubber into the alkyd chain. Although epoxide groups are reactive towards both hydroxyl groups and carboxyl groups, it has been reported that their reactivity towards carboxyl groups is relatively higher, allowing LENR50 to serve as polyol in the alkyd synthesis (Doszlop et al., 1978). The decrease in the intensity of peak at 872 cm^{-1} supports the conversion of the epoxide group during the alkyd synthesis, shown in Figure 4.26. Result from ^{1}H-NMR analysis agrees with the findings from FTIR analysis. ^{1}H-NMR spectra of LENR50 and 15R resins are shown in Figure 4.27. Compared to LENR50, the intensity of peak at 2.7 ppm which is attributed to the proton attached to oxirane ring decreased significantly in 15R resin. The emergence of peaks at 4.0 – 4.5 ppm in the spectrum of the alkyds correspond to the resonance of protons in the ester linkages formed from the esterification between the product of alcoholysis and diacids or LENR50.

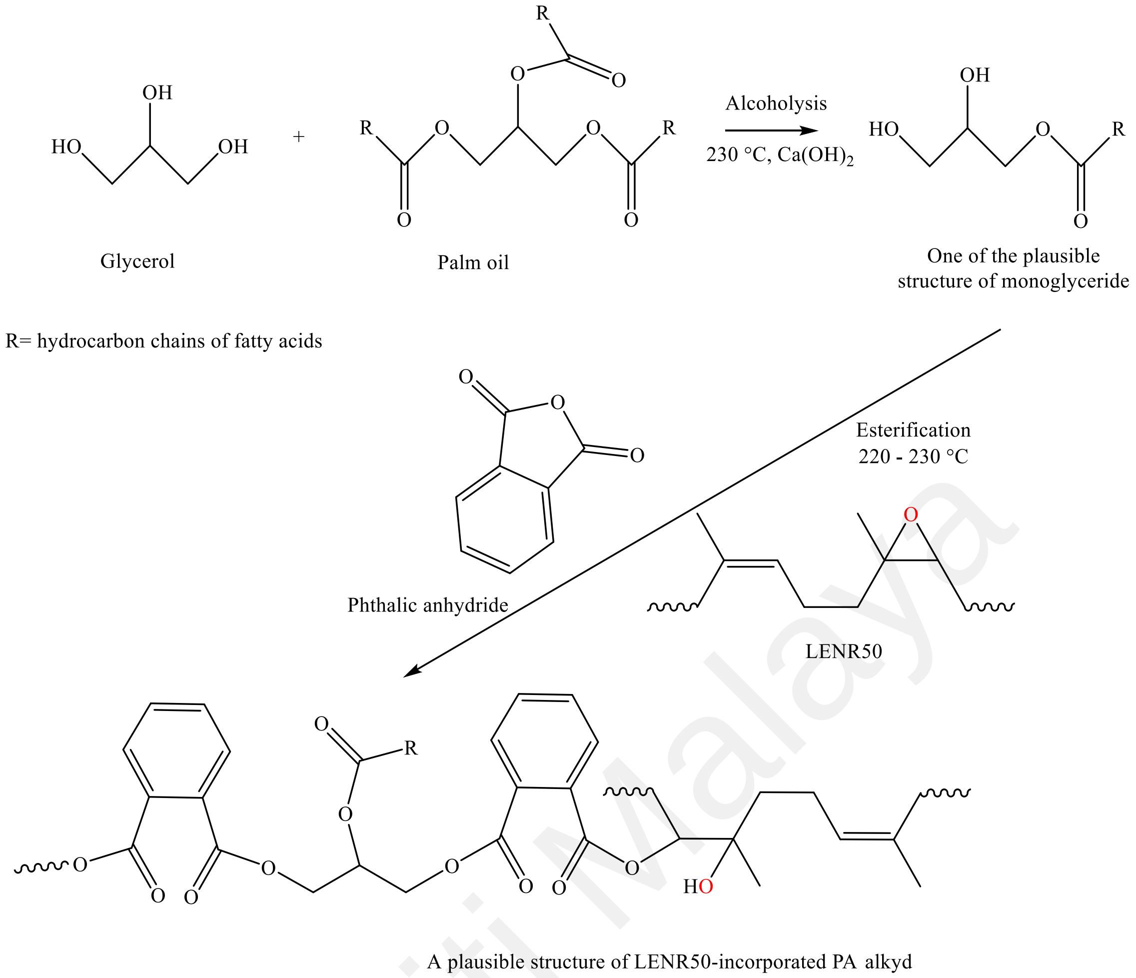


Figure 4.25: Proposed reaction in the synthesis of LENR50-incorporated alkyd resin

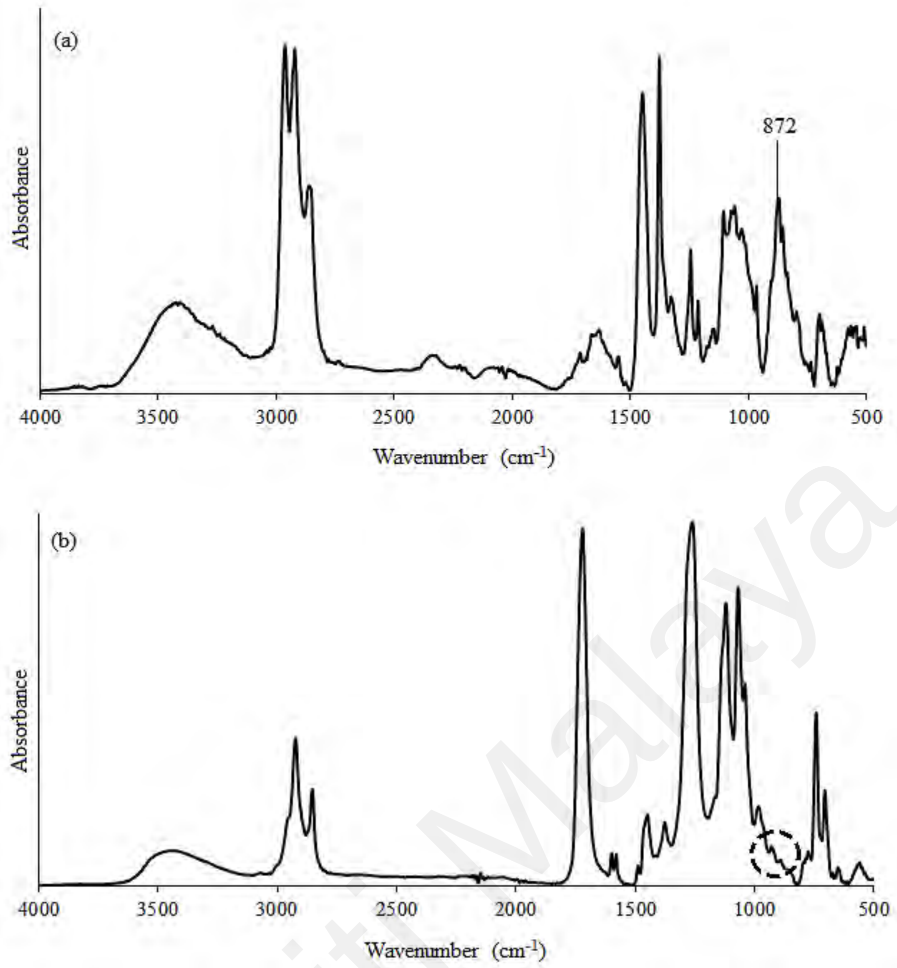


Figure 4.26: FTIR spectra of (a) LENR50, and (b) 15R resin

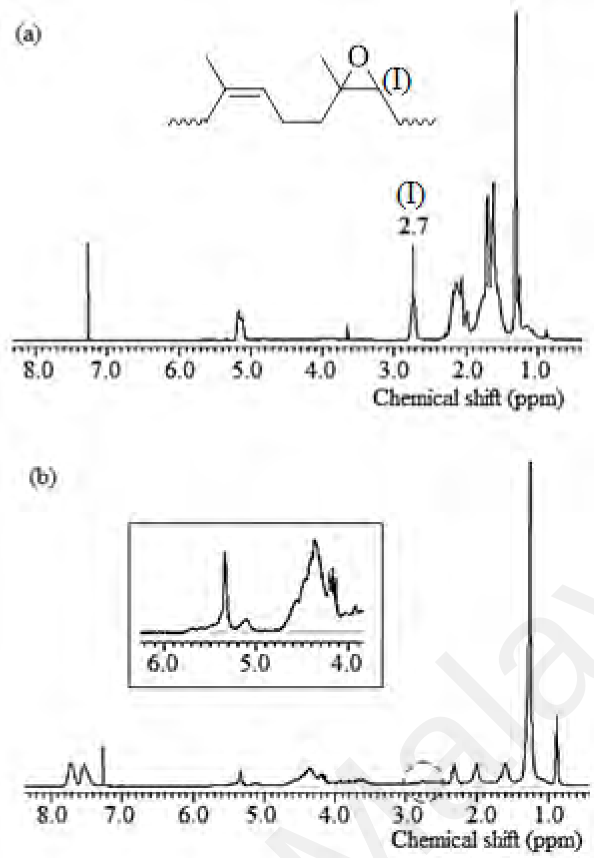


Figure 4.27: ^{1}H-NMR spectra of (a) LENR50 and (b) 15R resin

4.4.2 UV curing

A thin layer of alkyd coating mixture comprising of alkyd resin, reactive diluents, and UV photoinitiators were irradiated with UV light for curing to takes place. Curing of alkyd coatings involves the conversion of C=C double bonds present in the mixture, evidenced by the reduction in the intensity of peak at 5.3 ppm which is attributed to -C=C-H after the UV curing, shown in Figure 4.28. In contrast, peaks in the region 5.1 to 5.3 ppm are clearly visible in the ^{1}H-NMR spectra of the resin and LENR50 shown earlier in Figure 4.27. The drying time of alkyd resins are reported in Table 4.8. For control 100PA, it did not dry even after 15 mins of UV irradiation since the amount of unsaturation in the alkyd was limited, contributed solely by the small percentage of unsaturated fatty acids present in palm oil. Another control 20MA with higher amount of unsaturation due to presence of maleic acid in the formulation exhibited shorter curing time at 7 mins. LENR50-alkyd resins showed shorter drying time than controls ranging from 3 to 6 mins. Except 100PA which continued to remain tacky, other coatings turned to dry and hard films after UV curing.

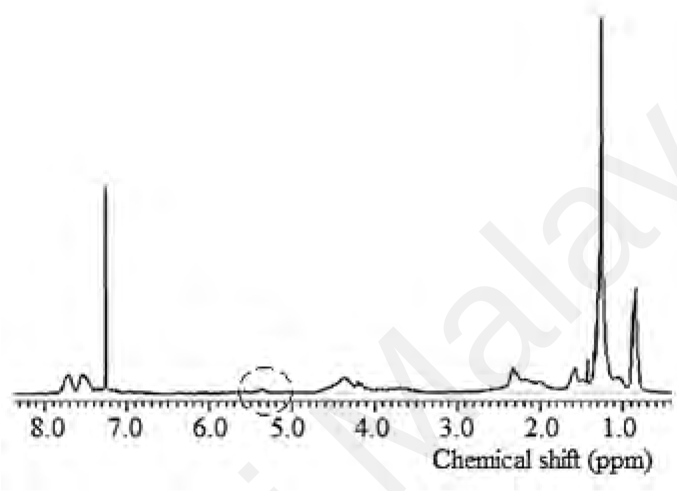


Figure 4.28: ^{1}H-NMR spectrum of UV-cured coating 15R

Table 4.8: Drying time of alkyd

Alkyd	Drying time under UV irradiation (min)
100PA	>15 (not touch dry)
20MA	7
5R	5.5
10R	4
15R	3
10R10MA	6

4.4.3 Film properties of UV-cured LENR50-alkyd coatings

(a) Gel content

Gel content was carried out to support the findings on the occurrence of crosslinking in alkyd coatings as well as compare the extent of crosslinking in coatings with different formulations. The result of gel content test is shown in Figure 4.29. Coating 100PA unsurprisingly recorded the lowest percentage of gel content, 8% since there was limited unsaturation for UV cure leading to almost complete dissolution. Coatings 5R, 10R and 15R possessed higher gel content compared to coating 100PA, which are 20%, 46% and 55% respectively, and the gel content increase with increase in the amount of LENR50 introduced into the alkyd system. This shows that the incorporation of LENR50 into the alkyd coating managed to promote greater extent of crosslinking and enable it to resist dissolution during the immersion. It is noteworthy that LENR50 by itself is very soluble in toluene, and the trend observed further suggest that the integration of rubber into the alkyd chain has taken place. The significant enhancement in the extent of crosslinking is presumably due to the C=C double bonds in LENR50 that took part in UV curing to form crosslinked network. The C=C from the rubber moiety increases the total amount of unsaturation available for crosslinking and reduces the need for unsaturated diacids in the formulation. In fact, coating 15R which was formulated without any unsaturated diacids exhibited higher gel content than coating 20MA. Coating 10R10MA, which was produced in combination of maleic acid and LENR50 also exhibited higher gel content than both controls.

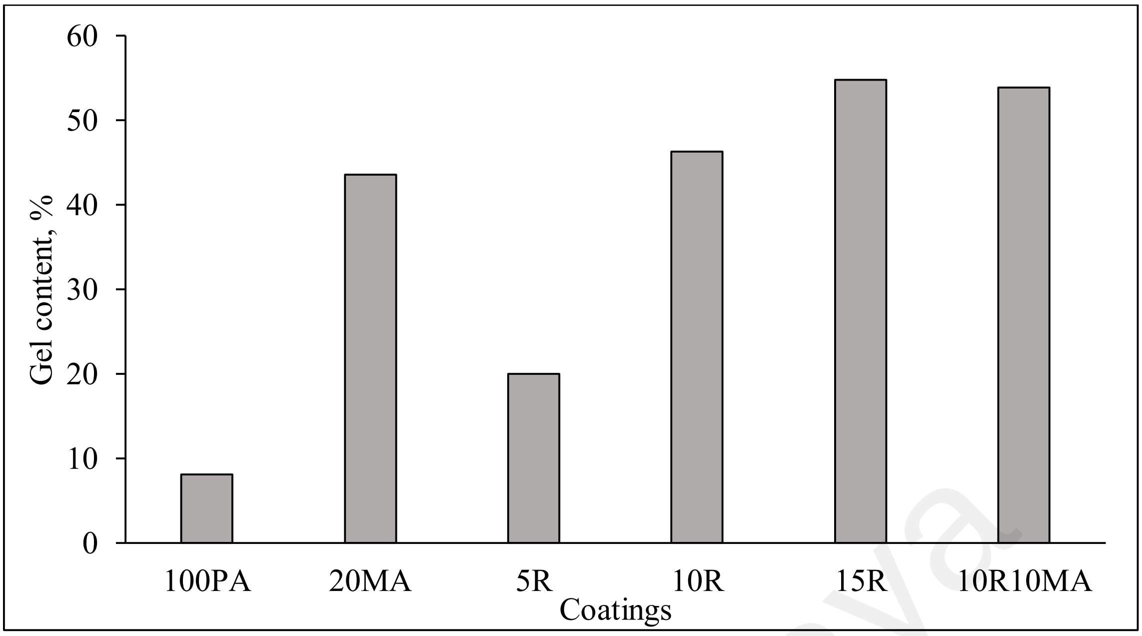


Figure 4.29: Percentage of gel content of alkyd coatings

(b) DSC thermal analysis

Thermal stability of the coatings was investigated by heating the samples in N_2 atmosphere from -90 to 120 ˚C. The DSC curves and glass transition temperature, T_g (shown in bracket) of coatings and LENR50 are shown in Figure 4.30. The incorporation of LENR50 in alkyd synthesis managed to increase the T_g of the resultant alkyd coatings. The midpoint of T_g of control 100PA was the lowest at -6 ˚C, followed by pristine LENR50 at -5.6 ˚C. Coatings 5R, 10R and 15R recorded higher T_g at 9 ˚C, 13 ˚C, and 16˚C respectively. Consistent with the gel content test result, the presence of LENR50 in the alkyd chain contributed to formation of greater extent of crosslinking in the UV cured coatings. Consequently, higher amount of energy was needed for the glass transition of the films to occur. The effect of LENR50 in promoting crosslinking in the coating is especially apparent from the comparison between coating 20MA and 10R10MA. The former recorded T_g at 9 ˚C, while coating 10R10MA recorded slightly higher T_g at 12 ˚C. Although the latter comprised of 50% less MA which is responsible to provide unsaturation for crosslinking during UV irradiation, the presence of LENR50 in the coating is able to compensate it, leading to both coatings having comparable T_g. Beside crosslinks, other factors that could affect T_g are the chemical structure of the coating, including the molecular weight, branching, backbone flexibility and the pendant groups which could affect the mobility of a polymer chain (Peng et al., 2020). The chain flexibility and freedom of main chain rotation of the UV cured coating is expected to be somewhat suppressed when the relatively large size LENR50 was integrated into the alkyd main chain.

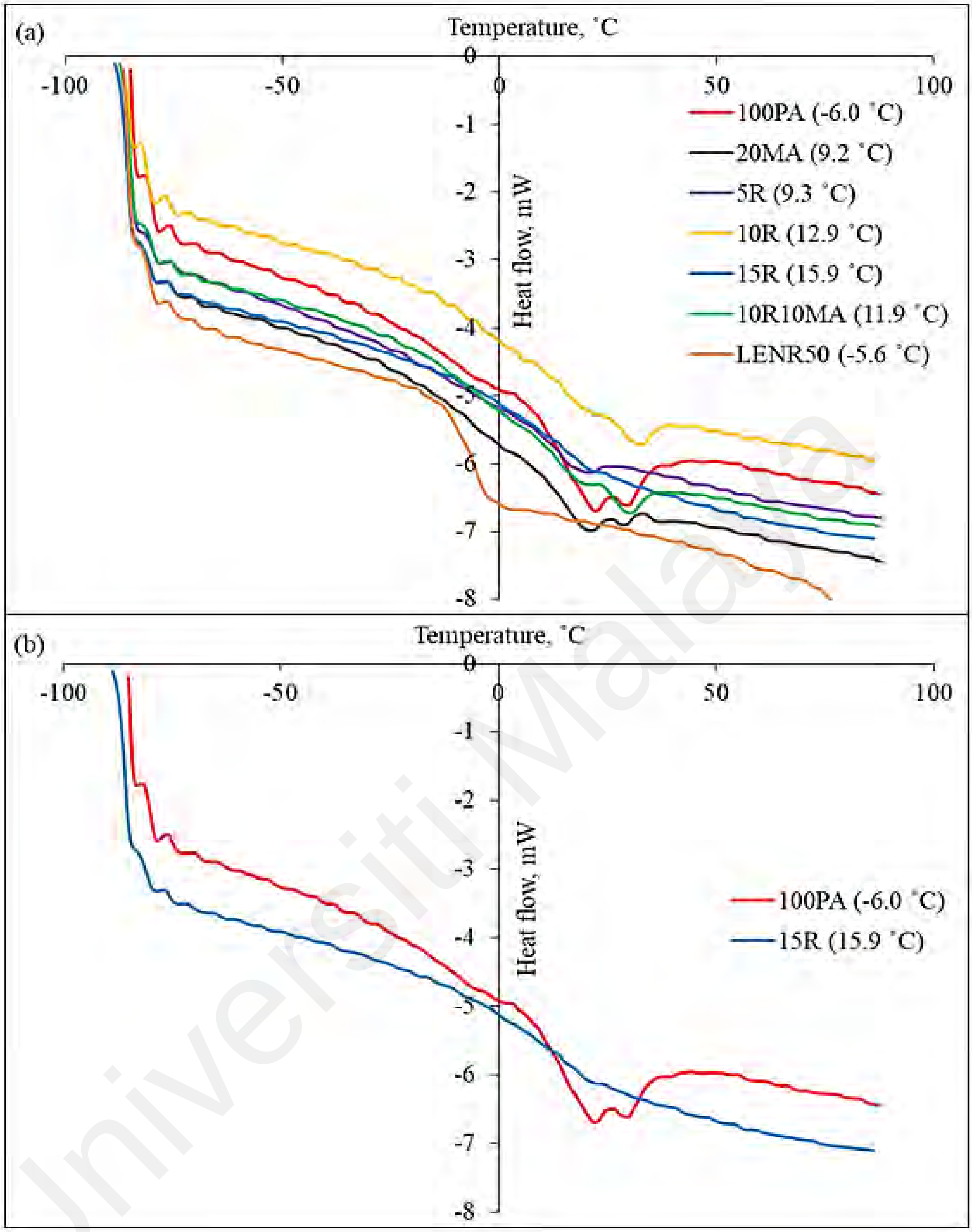


Figure 4.30: DSC thermogram of (a) all coatings and LENR50, and (b) coating 100PA and 15R

(c) Pencil hardness test

Pencil hardness test is one of the physicochemical property tests done on the cured coatings to investigate the coatings' hardness. The result of pencil hardness test is reported in Figure 4.31. All LENR50-alkyd coatings showed superior hardness compared to both of the controls with coating 15R and 10R10MA recorded the highest film hardness at pencil grade 2H. This could be due to the additional crosslinking contributed by LENR50. Control 100PA showed the lowest hardness at grade of 6B mostly caused by the little amount of unsaturation offered by palm oil. Control 20MA recorded better hardness that is 5 grades higher than 100PA, presumably due to the presence of MA which devote the unsaturation into the system.

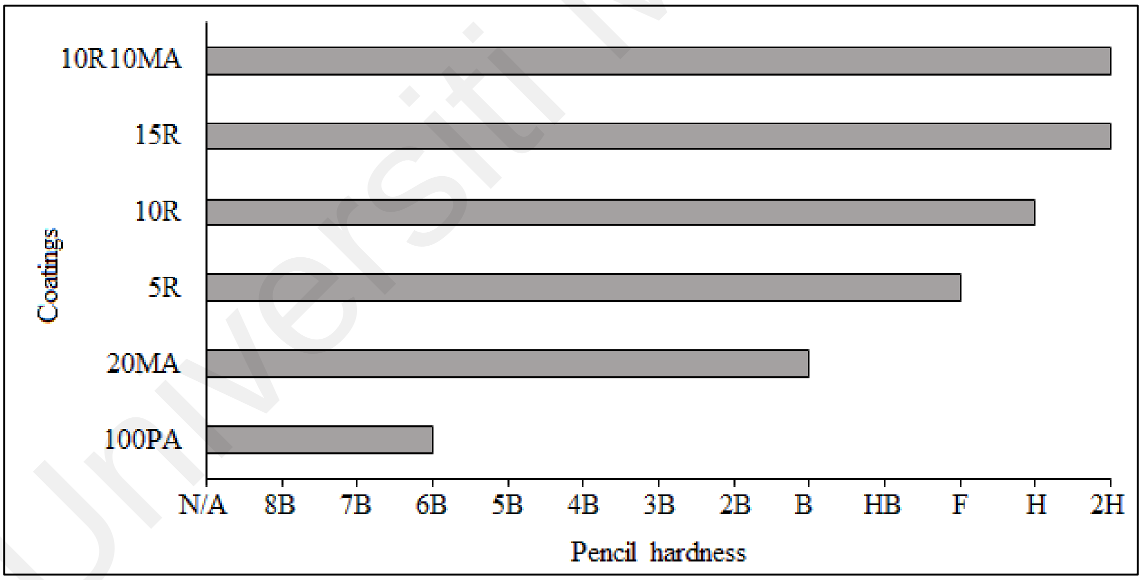


Figure 4.31: Pencil hardness grade of alkyd coatings

(d) Film adhesion test

Film adhesion was conducted on coatings to check their adhesion properties on metal surface and the result is tabulated in Table 4.9. Except for control coating 100PA which recorded 95% film removal, other coatings showed good to excellent film adhesion, recording grade 4B (< 5%) or 5B (0%). The control 100PA suffered almost complete film removal as the film was not integrated owing to lack of crosslinking, if any, in the coating. For the rest of the alkyd coatings, presence of various polar functional groups including ester, carboxyl, and hydroxyl groups warrants good film adhesion on the metal substrate.

Table 4.9: Percentage of film removal of alkyd coatings

Alkyds	Film removed, %	Adhesion grade
100PA	94.75	0B
20MA	3.69	4B
5R	1.13	4B
10R	0.00	5B
15R	2.46	4B
10R10MA	0.00	5B

(e) Solvent resistance test

Solvent resistance of coatings was investigated by rubbing the films with MEK solvent in total of 25 full cycles and the thickness of film removal is reported in Figure 4.32. Control coating 100PA experienced highest film removal, 0.013 mm. Film removal of all LENR50-alkyd coatings are in the range of 0.005 – 0.007 mm, slightly better compared to 0.009 mm of the control coating 20MA. The enhanced crosslinking promoted by the integrated rubber in the alkyd chain could have resulted with the observed improvement in solvent resistance. Again, this shows that inclusion of LENR50 in the alkyd formulation eliminates or reduce the need for unsaturated diacid monomers such as maleic acid in alkyd synthesis.

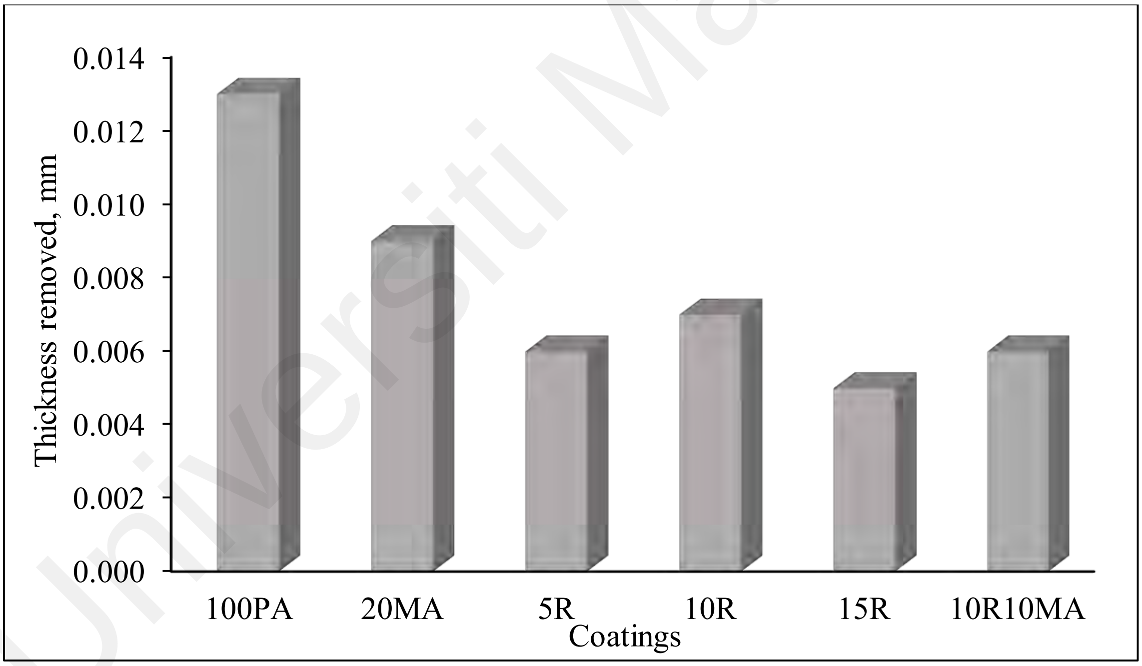


Figure 4.32: Thickness of alkyd coating films removed after 25 full cycle rubs with MEK solvent

(f) Water resistance test

Water resistance test was conducted on coatings by immersing them into distilled water for 24 hours and then observing the appearance of coatings. The appearance of coating after immersion is reported in Table 4.10. Coating 100PA experienced the most severe damage among all the coatings. Whitening and blistering occurred in coating 100PA and this condition was irreversible after conditioning in room. For other coatings, there were whitening appearances observed when they were removed from water immersion, however the whitening faded greatly after room conditioning for 1 hour. The whitening however did not completely disappeared, and the films appeared slightly translucent compared to their pre-immersion appearance, and this persist for the next 24 hours of room conditioning. In contrast to the water resistance of the epoxy coatings reported in the earlier section, alkyd coatings appear to have weaker water resistance. This could be due to the abundance of polar functional groups in the coatings have strong affinity to water molecule. Based on the observation, the water resistance property of LENR50-alkyd coatings were comparable to control coating 20MA and much superior to control 100PA.

Table 4.10: Observation on appearance of alkyd coatings after immersion in distilled water

Alkyds	Water resistance	
	Once removed from water	Conditioning after 1 hour
100PA	Whitening, blistering	Irreversible damage
20MA	Whitening	Whitening reduced significantly
5R	Whitening	Whitening reduced significantly
10R	Whitening	Whitening reduced significantly
15R	Whitening	Whitening reduced significantly
10R10MA	Whitening	Whitening reduced significantly

(g) Chemical resistance test

Chemical resistance test was conducted on coatings by immersing them into HCl, NaOH or NaCl solution for 7 days and the percentage weight change of the coatings is shown in Figure 4.33. In HCl immersion, coating 5R and 10R showed similar resistance to the control 100PA, while 15R showed slight improvement in acid resistance. All coatings experienced significant damage during the immersion in NaOH with respect to weight loss due to the abundant ester linkages which are susceptible towards alkaline hydrolysis. However, all LENR50-alkyd coatings recorded slightly lower percentage weight loss compared to both controls, with coating 15R recorded lowest weight loss in alkaline medium. Coating 100PA and 20MA experienced 69% and 68% weight loss whereas LENR50-alkyd coatings showed weight loss ranging from 49 – 55%. Albeit little, incorporation LENR50 into the formulation managed to improve the alkaline resistance of the alkyd coatings. In NaCl immersion, coating 100PA recorded 67% weight loss while coating 5R, 10R and 15R showed 39 – 45% weight loss. For qualitative observation, all coating films experienced whitening after immersion in HCl, NaOH and NaCl.

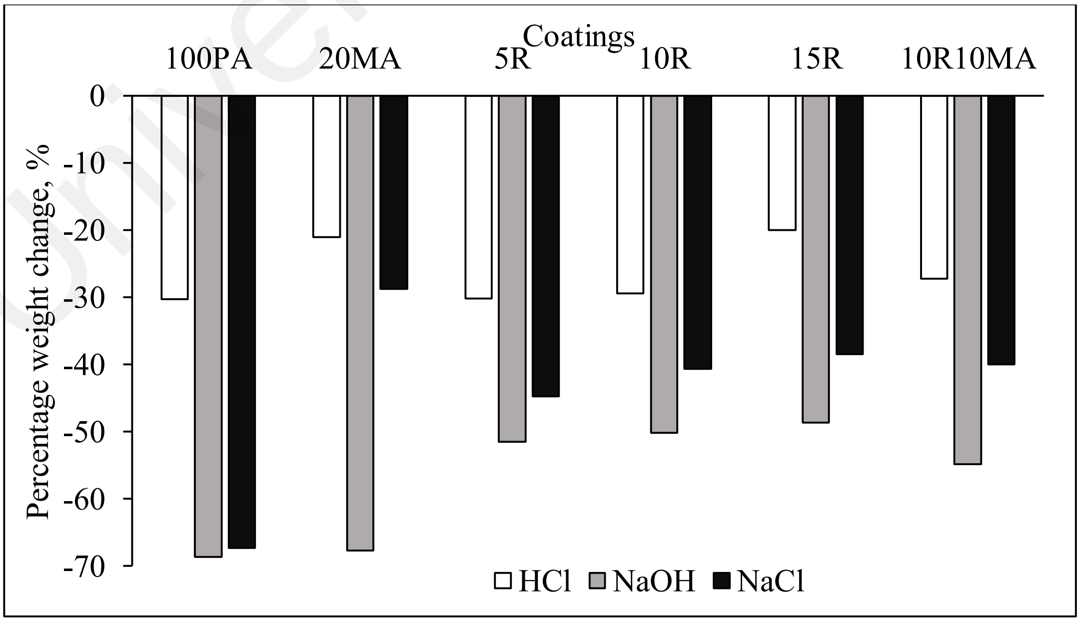


Figure 4.33: Percentage weight change of coatings after immersion in HCl, NaOH and NaCl

(h) Water contact angle

Water contact angle measurement was carried out to investigate the effect of introducing LENR50 in alkyd formulation on the hydrophobicity of the resultant alkyd coatings. The contact angles of coatings were shown in Figure 4.34. Both control pristine alkyd coatings were hydrophobic towards distilled water since they recorded contact angles > 90˚. For LENR50-alkyd coatings, all of them maintained hydrophobic surface, with contact angles in the range of 90 – 95˚. Based on the water contact angle result, the integration of LENR50 did not influence significantly the nature of coatings.

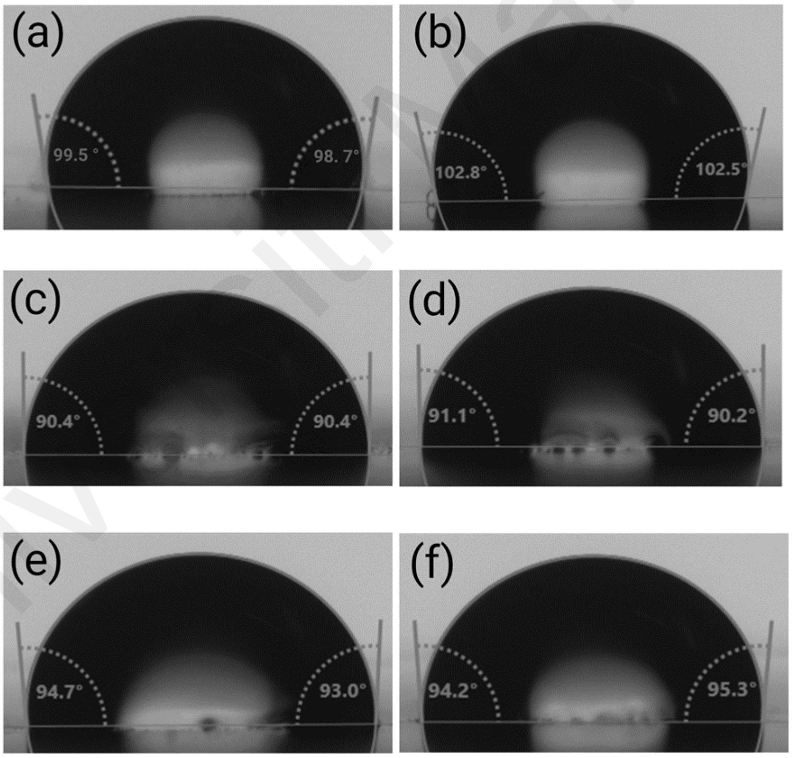


Figure 4.34: Water contact angle of (a) coating 100PA, (b) 20MA, (c) 5R, (d) 10R, (e) 15R, and (f) 10R10MA

(i) TGA thermal analysis

Thermal analysis using TGA was conducted on the coatings, and the results are shown in Figure 4.35. The TGA thermogram of LENR50-alkyd coatings are similar to pristine alkyd coatings, and the thermal stability of LENR50-alkyd coatings did not show any significant derivative from the controls. All coatings started to show apparent weight loss at temperature approximately 200 ˚C, and peak temperature corresponds to maximum rate of weight loss is above 350 ˚C. There was minimal weight loss prior to that, at below 100 ˚C which is attributed to evaporation of trace amount of trapped moisture and/or solvent.

From the 1st derivative TGA curve, the peak temperature that corresponds to maximum rate of weight loss is above 350 ˚C. From the 1st derivative TGA curve, the peak degradation temperature, T_p of coating 100PA is 380 ˚C while those for coating 5R, 10R and 15R are ranging from 359 – 371 ˚C. The slightly lower T_p recorded in the LENR50-alkyd coatings could be due to the traces amount of unreacted C=C double bonds contributed by LENR50 since unsaturation is one of the reactive sites for the initiation of chain decomposition reactions (Witkowski et al., 2015). Although there is reduction in peak degradation temperature, it is however not significant, and they remain suitable to be used as general purpose surface coatings.

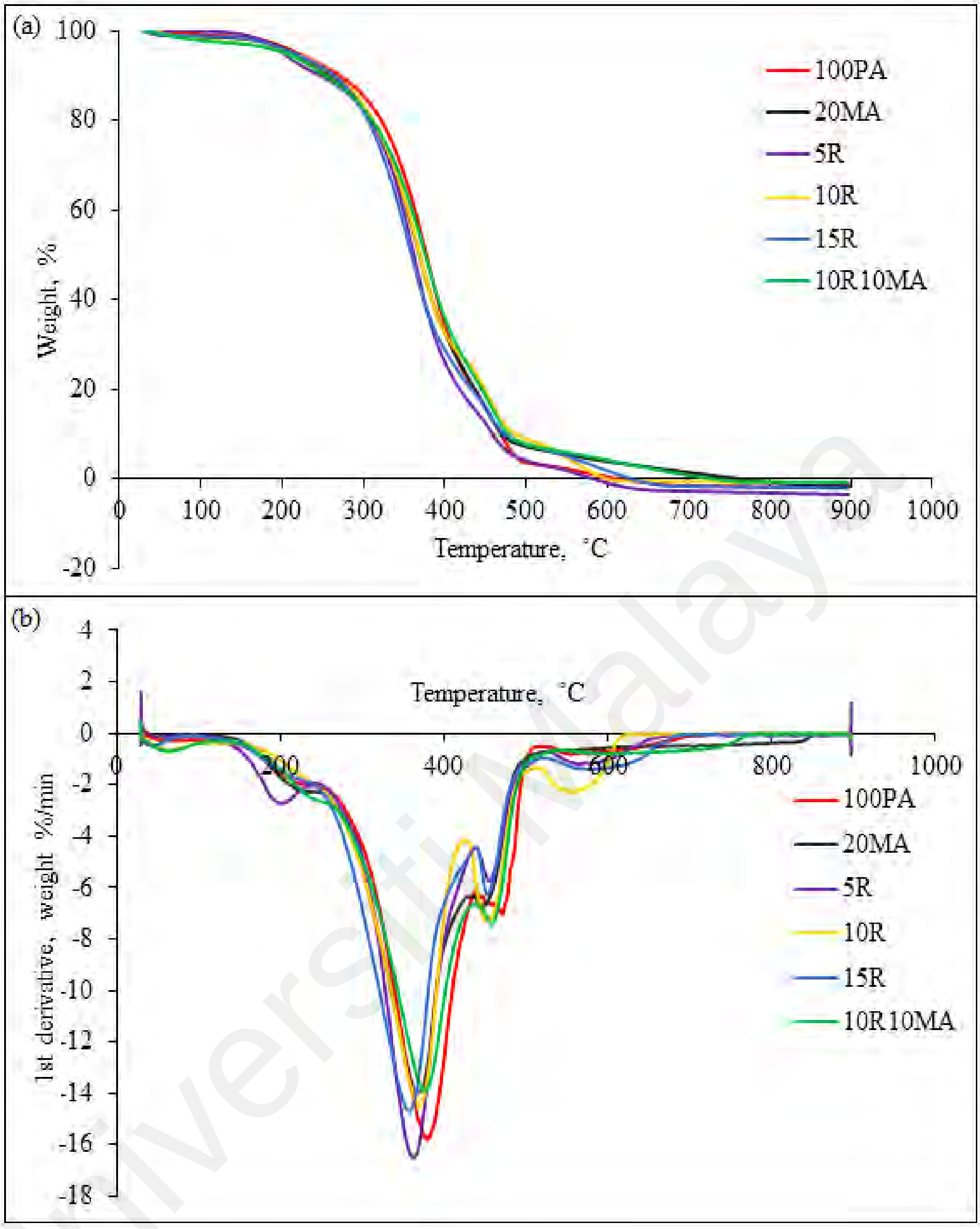


Figure 4.35: (a) TGA thermograms of alkyd coatings, (b) 1st derivative TGA thermograms of alkyd coatings

CHAPTER 5: CONCLUSIONS AND SUGGESTION FOR FURTHER RESEARCH

5.1 Conclusions

Epoxidized natural rubber has been utilized to produce three different coatings, in which two of them were epoxy coatings and another one was alkyd coating.

In epoxy coating, UV-degraded epoxidized natural rubber, UV-ENR25 which owed relatively low molecular weight, were used to serve as epoxy resin to react with hardeners, subsequently formed crosslinked film. Commercially available hardener, PETMP and natural-resourced hardener, tannic acid were able to react with UV-ENR25 and thermally cured into films with good physicochemical and thermal properties. The crosslinking reaction in UV-ENR25/PETMP and UV-ENR25/Tannic acid coatings was evident from the notable increase in the gel content. Crosslinking between UV-ENR25 and hardeners render films with good hardness and adhesion, increase the water and chemical resistance of films as well as improve the thermal stability. UV-ENR25/PETMP coatings shows slightly superior in term of physicochemical properties generally than that of UV-ENR25/Tannic acid coatings. UV-ENR25/Tannic acid coatings which were highly formulated with natural resources, causing them to be more susceptible to be broken down by microorganisms. Thus, the coatings experienced greater extent of biodegradation in the form of weight loss compared to the petroleum-derived control based on the result of soil burial biodegradation test. The overall performance of the epoxy coatings prepared are comparable with the commercial coatings, thus the applications of commercial coatings such as concrete floors, steel and metal are also applicable for the epoxy coatings prepared in this work. The biodegradable property of epoxy coatings prepared enable them to be applied on the disposable products such as food packaging.

As for alkyd coating, liquid epoxidized natural rubber, LENR50 was introduced as an alternative polyol to react with polycarboxylic acid. LENR50 which was chemically oxidative degraded and resulted with relatively low molecular weight compared to UV-ENR, is more favourable to integrate into bulk reactants system to serve as an alternative polyol. The mixture of rubber based alkyd resins, reactive diluent, photoinitiator and crosslinker was able to be UV-cured and formed smooth and dry film. The C=C double bonds in LENR50 have took part in UV curing to form crosslinked network in films, evident by the significant increase in gel content and glass transition temperature of coatings compared to controls. The presence of LENR50 has improve the film properties such as pencil hardness, film adhesion, water and chemical resistance. Thermal stability of LENR50-incorprated alkyd coatings are also satisfactory for general purpose surface coatings. The performance and properties of LENR50-incorporated alkyd coatings prepared are comparable with the commercial alkyd coatings thus they are appropriate to be used for the general application of commercial coatings such as architectural and wood application. LENR50-incorporated alkyd coatings are softer and showing inferior resistance in alkaline mediums compared to epoxy coatings prepared in this work. This shows the conformance with general epoxy coatings that normally exhibit hard and durable properties while alkyd coatings are softer and vulnerable towards alkaline medium due to the existence of abundant polyester linkage.

As concluded, natural rubber is a viable renewable resource that can be exploited in the development of surface coating. This practice help to reduce the dependency on epoxy resin derived from non-renewable fossil resources at the same time improve the biodegradability of films which is able to lessen the environmental problem generated from waste disposal. Other than that, the availability of LENR50 to integrate in alkyd chain has diversified the choice of natural-resourced polyol in alkyd cook. In addition, the additional C=C double bond offered by LENR50 increases the extent of crosslinking during UV curing, subsequently improve some of the film properties.

5.2 Suggestion for further research

In future, it would be interested to utilize UV-degraded epoxidized natural rubber with 50% mol of epoxidation to synthesis epoxy coating. UV treatment is favourable in production of epoxy resin because it is able to preserve most of the epoxide groups compared to other degradation methods. ENR50 solution should be able to be produced in suitable solvent before subjecting to UV irradiation. Owing to higher content of epoxide groups in ENR50 than ENR25, the extent of crosslinking formed in the films is expected to be higher and subsequently resulted with more desirable film properties. Besides, natural-resourced hardeners could be an interesting topic to be focused on. Discovering more crosslinking agents which are derived from renewable resources could diversify the choice of crosslinking agents as well as increase the percentage of natural raw material in coating formulation.

It could be interesting to introduce the liquid epoxidized natural rubber with 10% mol and 25% mol of epoxidation, LENR10 and LENR25 into alkyd synthesis and investigate the effect of incorporating LENR10 and LENR25 to compare with the one of LENR50. The film properties of resultant alkyd coating produced from alkyd resin formulated with different LENR could be varied as they carry different percentage of epoxide group and unsaturation. By keeping the amount of reactive site from polyol constant, the amount of rubber moiety and unsaturation vary from each LENR, vice versa. The amount of unsaturation in UV curing is vital for crosslinking to take place, the use of LENR10 could be expected to show higher extent of crosslinking. As the weight percentage of rubber is kept constant, the effect on extent of reaction between the epoxide group from rubber and the carboxyl group from diacids could be investigated. The highest amount of each LENR able to be introduced into the alkyd cook without occurrence of gelation, the ability of the LENR-alkyd resin to be dissolved in reactive diluent for rendering it to be UV curable, and the film properties exhibited by cured coatings is interesting to be studied.

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