CHARACTERISTIC OF RENEWABLE POLYMER INCORPORATED WITH STABILIZER TO CHARACTERIZE THE ENDURANCE OF ULTRA VIOLET IRRADIATION EXPOSURE

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In the name of ALLAH, Most Gracious, Most Merciful.

This thesis especially dedicated to;

My beloved husband
~Ahmad Azirun Bin Ab. Rahman~

My beloved father
~Mat Hassan Bin Bakar~

My beloved late mother
~Raja Nab Binti Raja Keckek~

My supportive supervisor
~Assoc. Prof. Dr. Anika Zafiah Binti Mohd Rus~

~My friends~

~Thank you for everything~
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ABSTRACT

Waste vegetable from palm oils are most abundant biological sources and important raw materials for production of renewable polymer because of their versatility with high possibility to modify the chemical structure of triglycerides and its derivatives. In this study, waste vegetable oil was synthesized and crosslink with polymethane polyphenyl isocyanate, distilled water and titanium dioxide (TiO₂) as filler to form renewable polymer. Two fabrication method was used; (i) manual casting which produced renewable polymer foam (RF) and (ii) compression moulding at 90 °C based on the evaporation of volatile matter and the product is known as compressed renewable polymer (CR). Composites of RF and CR is known as RFC and CRC respectively. The physical, vibration and damping properties are measured to determine the endurance of renewable polymer to UV irradiation exposure. The morphological structure and porosity of renewable polymer shows no significant changes after UV irradiation exposure. As the loading of TiO₂ increased (up to 10 % of monomer weight), the thermal degradation temperature were increased at three different decomposition stages. The vibration transmissibility of renewable polymer based on resonance peak, resonance frequency and attenuation frequency at different thickness were shifted to lower frequency range from 23 Hz to 21 Hz with increasing of UV irradiation exposure time. Meanwhile, the damping property of 10 % and 5 % TiO₂ filler loading (RFC₁₀ and CRC₅) gives maximum values of 0.5 and 0.6 respectively with increasing of UV irradiation exposure time. This is due to the potential of RFC₁₀ and CRC₅ to dissipate more energy in foam block system. Hence, TiO₂ act as UV stabilizer enhance the photostability of renewable polymer which exhibit endurance to prolonged UV irradiation exposure.
ABSTRAK

Sisa minyak sayuran berasaskan kelapa sawit adalah kaya dengan sumber biologi dan merupakan bahan mentah untuk menghasilkan produk polimer yang diperbaharui kerana sifat kepelbagainya yang mempunyai potensi yang tinggi untuk mengubah struktur kimia pada trigiserida dan terbitannya. Dalam kajian ini, polimer yang boleh diperbaharui berasaskan sisa minyak sayuran telah disintesis dan bersambung silang dengan *polymethane polyphenyl isocyanate*, air suling and titanium dioksida (TiO$_2$) sebagai bahan penambah untuk membentuk polimer yang diperbaharui. Dua kaedah pembuatan telah digunakan iaitu (i) penuangan manual yang menghasilkan buih polimer yang diperbaharui (RF) dan (ii) mampatan panas pada suhu 90 °C berdasarkan penyelisihan bahan yang tidak menentu dan menghasilkan polimer mampat yang diperbaharui (CR). Komposit bagi RF dan CR masing-masing dinamakan sebagai RFC and CRC. Sifat fizikal, getaran dan redaman diukur untuk menentukan ketahanan polimer yang diperbaharui terhadap pendedahan sinaran UV. Struktur morfologi dan keliangan pada polimer yang diperbaharui menunjukkan tiada perubahan yang ketara selepas pendedahan kepada sinaran UV. Merujuk kepada peningkatan TiO$_2$ sebagai bahan penambah (sehingga 10 % daripada berat monomer), suhu penguraian haba meningkat pada tiga peringkat penguraian suhu. Sifat pengalihan getaran oleh polimer yang diperbaharui berdasarkan kepada puncak resonans, frekuensi resonans dan pengecilan frekuensi diuji pada ketebalan yang berbeza dan memberikan anjakan ke frekuensi yang lebih rendah dari 23 Hz kepada 21 Hz dengan peningkatan masa pendedahan sinaran UV. Walau bagaimanapun, sifat redaman pada 10 % dan 5 % bahan penambah TiO$_2$ (RFC$_{10}$ dan CRC$_{5}$) masing-masing memberikan nilai maksimum iaitu 0.5 dan 0.6 dengan peningkatan masa pendedahan sinaran UV. Ini disebabkan keupayaan RFC$_{10}$ dan CRC$_{5}$ untuk melepaskan banyak tenaga semasa dalam sistem blok busa. Oleh itu, TiO$_2$ bertindak sebagai penstabil UV yang mana meningkatkan kestabilan foto bagi polimer yang diperbaharui dengan ketahanan terhadap pendedahan sinaran UV yang berpanjangan.
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<td>ASTM</td>
<td>American Society for Testing Materials</td>
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<td>ATR</td>
<td>Attenuated total reflection</td>
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<td>CO₂</td>
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<td>CR</td>
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<td>KOH</td>
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$R$ - Gas constant
$T$ - Absolute temperature (K)
$RM$ - Renewable monomer
$RF$ - Renewable polymer foam
$RFC$ - Renewable polymer foam composite
$UV$ - Ultraviolet
$UV-Vis$ - Ultraviolet visible
$WO$ - Waste vegetable oil
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CHAPTER 1

INTRODUCTION

1.1 Introduction

Plants are the most important renewable resource. It was estimated that around 120 billion tonnes of carbon in biomass, equivalent to over 80 billion tonnes of oil, are generated globally yearly by photosynthesis. From the chemical point of view, about 75 % of biomass is carbohydrates, 20 % lignin and about 5 % of oils and other constituents (Nieto, 2011). Figure 1.1 demonstrates the life cycle of vegetable raw materials after their transformation into products. These products are then be used before discarded. The produced sub-products should be assimilated for the biomass, closing the cycle or recycled in order to minimize waste.

Figure 1.1: Life cycle of products derived from biomass (Nieto, 2011)
Recently, the natural vegetable oils are consider to be one of the most important classes of renewable source and has high potential to synthesis and become a new polyol sources for polyurethane and can be replaced for commercial polyol in manufacturing polyurethane. The synthesis of polymeric materials from renewable resources has been and remained until this date as one of the greatest challenges for the scientific community. Nowadays, considering the economical and environment concern, together with an increasing dependence on petroleum resources, have reinforced the need of using sustainable renewable resources.

The developing of renewable resources such as soybean oil, canola oil, rapseed oil, corn oil, palm oil, sunflower and linseed oil for polymer industries become highly desirable for both economic and environmental reasons (Rus, 2010). Bio-polyol from vegetable oil which is non-petroleum based that is renewable, less costly and more eco-friendly was applied as an alternative to reduce consumption of petroleum. Among different natural oils, the vegetable oils from palm oil are widely explored for bio-polyol synthesis due to the main components existing in vegetable oils which are triglycerides. These triglycerides are available as platform chemicals for polymer synthesis. The several reactive positions of triglyceride vegetable oil which are saturated and unsaturated fatty acids are useful in many synthesis transformations and become a new polyol source (Ronda et al., 2011).

In particular polyol and it's crosslinker; isocyanate in which the solidify polymer known as polyurethane is mainly depends on the types of polyol such as functionality and hydroxyl value. Thus, the polyurethane elastomer which was successfully synthesized using vegetable oil derived from polyol revealed the improvement of thermal stability and oxidation resistance (Zhang et al., 2007). Meanwhile, polyurethane (PU) foams with versatility as an engineering materials find a wide range of applications due to it’s properties which can be readily tailored by based on composition of their components. However, the main market for polyurethane foam is in polymeric foam, which are flexible and rigid. Flexible polyurethane foams are two predominant application forms of polyurethane with coatings, sealants, elastomers, and adhesives being other common forms of applications. Generally polyurethane foams are one of the major products from urethane material. The characteristic of polyurethane foam can be changed via adjusting the chemical composition of the raw materials.
1.2 Background of study

Nowadays, nearly all polymer materials are produced based on crude oil as feedstock. Polymers from renewable resources have attracted an increasing amount of attention over the last two decades; predominantly due to two major reasons which are environmental concerns and the realization that our petroleum resources are finite. Polymers from renewable resources can be classified into three groups such as natural polymers, synthetic polymers from natural monomers and polymers from microbial fermentation (Yu et al., 2006). Like numerous other petroleum-based polymers, many properties of polymer from renewable resource can also be improved through blending and composite formation.

Vegetable oils are consider to be one of the most important classes of renewable resources because of the wide variety of possibilities for chemical transformations, universal availability, low price and possible to modify the chemical structure of triglycerides and it derivatives (Miao et al., 2013). The term of waste vegetable oils includes all vegetable oil such as soybean oil, peanut oil, sunflower oil, linseed oil, coconut oil, cottonseed oil, canola oil, corn oil, safflower oil, walnut oil, castor oil, tung oil, etc. Among the different natural oils, the waste vegetable oils from palm oil is widely explored for bio-polyol synthesis to prevent pollution of waterways and clogging private and municipal drain systems, restaurants and other food preparation.

Waste vegetable based palm oils are most abundant biological sources and important raw materials for the production of bio-based polyurethanes. The main components existing in waste vegetable oil are triglycerides with saturated and unsaturated fatty acids useful in many synthesis transformations and become new polyol sources (Ronda et al., 2011). In polymer industry, waste vegetable oils which represent a major potential source of chemicals have been utilized as an alternative feedstock for bio-monomers (Narine et al., 2007; Rus et al., 2008; Rus et al., 2009; Hassan et al., 2013).

Synthesis of bio-monomer is started with the preparation of catalyst to generate the epoxides from the unsaturated fatty compounds of the waste vegetable oil. The condensation process comprises of acid-catalysed ring-opening of the epoxides to form polyols.
The formation of renewable polymer foam is followed the same general reaction of isocyanate with bio-monomer and both of which are derived when polymerization reactions occur similar to nearly all polymeric materials (Lim et al., 2008). This polymer is addressed as polyurethane (PU) foam are versatile engineering materials which find a wide range of applications. Generally PU foam is one of the major productions from urethane polymer structure. The forming process of renewable polymer foam consists of three basic stages such as bubble initiation, bubble growth and cell opening. The bubble initiation was initially introduced by physically bending air into the mixture. The bubble growth occurs when the gas diffused and expands the gas phase due to increasing the forming temperature. The gas may originate from sources such as a gas involved by water reaction, blowing agents, carbon dioxide and surfactant. The heat generated during the reactions due to exothermic process play an important role in expansion to form a cellular structure (Klempner & Sendijarevic, 2004). The bubble continued to grow and it will begin to open the cell to produce renewable polymer foam.

One of the important property of polymer foam are vibration and damping characteristic in the development of foam block system. The foam block system is crucial in research work on dynamic response of the foam at different level of compression and excitation in single degree of freedom. In other hand, this is to identify the viscoelastic properties through foam modeling designed. This concept is contributed to seat-occupant system. The system can be applied in wide range of polymeric material for foam dynamic response measurement and its characterization based on vibration of kinetic energy, potential energy, and energy loss (damping) (Singh et al., 2003; Joshi et al., 2010). The vibration of the systems which is involved its potential energy to kinetic energy and from its kinetic energy to potential energy. If the system is damped, some energy is dissipated in each of the cycle of vibration and must be replaced by an external source if the state of steady vibration is to be maintained.

Wider impression range of performance characteristics is to enhance the service life which contributed from the appropriate choice of stabilizers. The best selection of stabilizers depends on the specific production conditions, end user environment and fundamental degradation mechanism of the polyurethane components. Degradation of both the polyols and urethane components changed the physical and mechanical properties of the polyurethane. Urethane is susceptible to
degradation by free radical pathways induced by exposure of heat or ultraviolet light (UV).

Meanwhile, polymer degradation in broader terms includes biodegradation, pyrolysis, oxidation, and mechanical, photo- and catalytic degradation (Yousif et al., 2011). The photo degradation was occur due to UV radiation of polymer makes up less than 5 % of sunlight energy mainly of visible and infrared light. The UV radiation spectrum is divided into three range which is UV\textsubscript{A} (315-400nm), UV\textsubscript{B} (290-315nm) and UV\textsubscript{C} (100-290nm).

In order to enhance the photo stability of renewable polymer foam the pretreatment of physical property of renewable polymer foam is needed which include UV stabilizer filler such as titanium dioxide (TiO\textsubscript{2}). TiO\textsubscript{2} is also an inorganic pigment and used as an additive of excellent UV screener to reflect the light away from the polymer surface (Robinson et al., 2011). This pigment is important in polymer as an inner screen for photo products and limited the photo oxidative phenomena. It is also can be used to reduce cost, reinforcement, hardening, improving slip and storage stability. Furthermore, TiO\textsubscript{2} has been recognized as the most important photocatalyst for the degradation of many organic pollutants in water and air (Hazarika & Maji, 2014).

1.3 Problem Statement

In recent years, the consumption of crude oil is 85 % was used for energy generation; fuel for transportation (45 %), electrical generation and heating (42 %) and plastics (13 %). In the plastic industry, all thermosets are made up of 85 % of the total plastic industry and polyurethane represents 5 % of the total plastic market (Sin, 2008). Coupled with the recent escalating price of petroleum reaching USD 53 per barrel (Crude oil price forecast, 2015), it is also hoped the findings of the present study will be utilized to replace some petroleum based plastics and thus, reduce the dependence and consumption of petroleum oil. Furthermore, the current intensive awareness on environment, green and environmental friendly products are gaining attention and their demand is ever growing.

Moreover, in Malaysia, Small Medium Entrepreneurs (SME) has problems with the overloaded waste vegetable oils. Waste vegetable oil has proven to be a
problematic material, and most people do not know how it should be managed. Certainly, it should not be poured down the drains of the kitchen sink. It can clog the sanitary sewer system and causing costly backups. Furthermore, the lack awareness about proper waste vegetable oil management has been concern due to the environmental pollution particularly land and water pollution, and reduce the hazardous effect to human health. Realistically, in term of health awareness, abundance and low cost, renewable polymer foam from waste vegetable oil with relatively simple processing is the alternative recycling method to provide a good solution to the society.

Related to these issues, a study was carried out to investigate the recycling of waste vegetable oil. This process is started by converting into renewable monomer as polymer feedstock in order to substitute the polymer based petroleum. Hence, the use of renewable resources and its composite in the preparation of various industrial materials has been revitalized because of the environmental concerns. One of the important classes of polymer is foam based application due to light weight, resiliency and energy absorption properties that make flexible polymer foams is the key material in automotive and other transportation equipment manufacture. Therefore, in this study, the important characteristic of properties which based on polymeric material of solid or foam and its derivatives is vibration and damping application.

Damping capacity of a polymer composite is the fundamental property for designing and manufacturing structural component in dynamic and automotive applications such as car cushion, car dashboards, door panels and engine casings are produced by natural fiber and petroleum based. Materials with high damping properties are very desirable to suppress mechanical vibration and transmission of waves, thus decreasing noise and maintaining the stability of structural system (Ben et al., 2013).

Variation of processing technique to reduce porosities which benefited to passenger comfort based on (a) removing or isolating the source of vibration, (b) changing the mass or stiffness of a structure so that the natural frequency are changes and (c) absorbing (damping) of the vibrational energy. As a comparable of this damping and vibrational energy property, it is considered to resolve by using renewable polymer from sustainable resources.

However, degradation of renewable polymer occurs when exposed to the environment under sunlight and UV irradiation exposure is important criteria to be
considered in the damping and vibrational application. The limitation used of polymers is due to susceptibility to attack by oxygen, heat and light, thereby reduces the mechanical properties. In protecting the polymer from ultraviolet (UV) irradiation effect, it is recommended to use UV stabilizer such as TiO$_2$. TiO$_2$ has good UV blocker and is very attractive in practical applications because of advantages as nontoxicity, chemical stability at high temperature and permanent stability under UV exposure. This is the effective ways as stabilization process which most of the polymers are easily deteriorate, discolor and become brittle. Due to this, the characterization of damping and vibration is determined to evaluate the stability after the UV irradiation process.

1.4 Hypothesis of research

The hypotheses considered in this research are:

i. Synthesis of renewable monomer from waste vegetable oil by epoxidation and hydroxylation process with crosslinker to produce renewable polymer foam.

ii. Renewable polymer foam is characterized by functional group and optical UV-Vis after UV irradiation exposure and by incorporation with TiO$_2$ filler as UV stabilizer to improve the photostability property.

iii. Vibration and damping characteristic of renewable polymer foam, compressed renewable polymer and its composite is not significantly changes after UV exposure. This is important to stabilize the renewable polymer properties in order to enhance the photostability by UV stabilizer.

iv. The mechanical properties of renewable polymer and its composite are not significantly changed after UV irradiation exposure. This is important since this properties leads to the ability of polymer to dissipate vibration and damping energy through absorption on the polymer structure.
1.5 **Objective of research**

The main objective of the research is to develop polyurethanes from waste vegetable oil as renewable resources with endurance to UV by incorporate UV stabilizer for damping and vibration characteristic. A series of studies was conducted to achieve specific objectives as follows:

i. To synthesize renewable monomer from sustainable resources based on waste vegetable oil by condensation method.

ii. To develop the renewable polymer foam (RF), compressed renewable polymer (CR) and incorporation with UV stabilizer at different percentages of titanium dioxide (TiO$_2$) namely as renewable polymer foam composite (RFC) and compressed renewable polymer composite (CRC).

iii. To determine the physical properties, vibration and damping characteristic of renewable polymer foam (RF), compressed renewable polymer (CR), renewable polymer foam composite (RFC) and compressed renewable polymer composite (CRC) endurance to prolonged UV light irradiation exposure.

1.6 **Scopes of research**

The scopes of research are as follow:

i. Collection of waste vegetable oil from Small Medium Entrepreneur (SME) is located at Parit Raja, Batu Pahat, Johor.

ii. Synthesis of waste vegetable oil by in-house catalyst preparation at E1 (Sustainable Polymer Engineering, AMMC) to generate the epoxies from unsaturated fatty compound.

iii. Developing of RF and it’s composites (RFC) doped with TiO$_2$ filler loading using simple casting method. Meanwhile, CR and CRC is fabricated by simple casting method and then hot compression moulding technique to reduce thickness and porosity.

iv. The physical characteristics of RF, CR, RFC and CRC are determined by density, porosity, thermal stability, chemical bonding, morphological structure
and UV absorbance wavelength and the mechanical property such as compressive strength, vibration transmissibility and damping ratio.

v. UV exposure treatment of RF, CR, RFC and CRC at 250 hours, 500 hours, 750 hours and 1000 hours using Accelerated Weatherometer at 50 °C. This is to study the endurance of UV irradiation exposure towards of physical and mechanical characteristic of the RF, CR, RFC and CRC.

vi. The measurement of damping characteristic of RF, CR, RFC and CRC using vibration transmissibility test is conducted at 0.1 g and 0.15 g for acceleration base excitation and 1 mm and 1.5 mm for displacement base excitation at a frequency range of 15-25 Hz.

1.7 Significant of research

Corresponding to the objectives, some important points could be expressed as significant of research and professional usage as well as automotive application. There are four prominent contributions that can be provided from the result of this research.

i. This research is intended to improve the properties of renewable polymer doped with TiO₂ as a UV stabilizer with endurance to UV irradiation for the applications in absorbing vibration especially on motor vehicle in maintaining the stability of structure system.

ii. This research will determine whether this is able to increase the polymer mechanical properties of RF, CR, RFC and CRC that serves as a vibration or damping in dynamic of transmission waves.

iii. The alternative recycling method is comprises of hot compression technique for polymer generated from recyclable renewable resources.

iv. RF, CR, RFC and CRC may reduce the cost in various foam applications through the use of waste vegetable oils for renewable polymer foam and contributes to a friendly environment, sustainability and adds to green technology.
1.8 Thesis organization

The present thesis comprised of six chapters that were organized in order to address the objectives as referred to in section 1.5 which are:

• Chapter 1: The description of research overview is discussed. The problem statements, research objective, scope of the research and the research contributions are described. The overall contents of the thesis are also summarized in this chapter.

• Chapter 2: The basic theory to support the implementation of the background research work is discussed in this chapter.

• Chapter 3: The details of the experimental works are presented. The samples preparation, fabrication method and equipment used in the research activities are described. The parameter or the specific experiment such as density, SEM, TGA, FTIR, UV-Vis, compression test, damping and vibration are explained.

• Chapter 4: The spectroscopic characterization of starting oil, renewable monomer and mechanical and physical property of renewable polymer of RF, CR, RFC and CRC are presented and discussed as followed the objectives of the research work.

• Chapter 5: The analysis on the photostability or the endurance to UV light of renewable polymer specimen after UV irradiation exposure is described.

• Chapter 6: The conclusions derived from experimental and investigations are presented. The future works as recomendations are also stated in this chapter.
CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

This chapter provides a literature review of some significant contribution related to development of renewable polymer from waste vegetable oil for vibration and damping characteristic. Establishing a framework for the present study, the basic concepts involved the synthesis of renewable monomer from waste vegetable oil, renewable polymer foam and its composite development, titanium dioxide (TiO$_2$) as UV stabilizer, degradation of polymer, vibration and damping characteristic, mechanical and physical properties are review.

2.1 Polymer

A polymer is a macromolecule composed of a combination of small units that repeat themselves along the long molecule. The small starting molecules are call monomers and the unit which repeats itself along the chains is called the repeating unit. In general, polymer chains have several thousand repeat units (Hasirchi et al., 2011). However, the length of the polymer chain is specified by number of repeating units in the chains and this number is namely as degree of polymerization. Hence, polymer can be synthesis from hundreds of monomer in numerous combinations in very different forms ranging from solid elastomers to fiber, from films to sponges and from tubes to gels.
Polymer can be classified in many different ways depending on their various properties according to the origin, polymerization process, structural form of the chains, structure, molecular weight, thermal behavior, composition of the main backbone of the polymer and arrangement of the repeating units. The origin polymer is divided into three groups: (1) natural polymer such as cotton, starch, proteins, and wool; (2) semi-synthetic polymer such as natural rubber, chlorinated natural rubber, nitrocellose, carboxy methyl cellulose and cellulose acetate; and (3) synthetic polymer such as nylon, poly (vinyl chloride), polystyrene, polytherimide and polyethylene (Karak, 2012). On the other hand, polymer obtains from natural resources such as vegetable oils, animal fats, and insert are known as bio-based polymer (biopolymer).

In general, for engineering purpose, the most useful classification is based on their thermal response such as thermoplastic and thermoset polymer. Thermoplastic polymer are linear branched chains containing polymers and they soften and flow when the temperature is increased. Upon cooling the thermoplastic polymer is harden and solidify forming the product following the mold shapes. Thermoplastic also can be reshaped with further application of heat and pressure. Meanwhile, thermoset polymer is the processing with crosslinking reaction take place upon increase of temperature and modify in the shape of the mold. Therefore, it cannot be melted, reshaped with the application of heat and decompose at high temperature.

2.2 Polymer from renewable resources

Developing renewable resources such as soybean oil, canola oil, rapeseed oil, corn oil, palm oil, sunflower oil and linseed oil become highly desirable for both economic and environmental reasons for polymer industry (Rus et al., 2010). They are considered to have high potential to synthesis and become a new polyol sources for polyurethane and can replace the commercial polyol in the manufacturing of polyurethane. The polyurethane elastomers which are successfully synthesized using vegetable oil to derive polyol revealed the improvement of thermal stability and oxidation resistance (Zhang et al., 2007).

The vegetable oils are remarkable renewable resources particularly abundant and cheap. Due to these reasons, the bio-polyols synthesized from vegetable oils are attractive replacements for producing green polymer foam. Bio-based biopolymers
based on renewable resources are divided by natural or synthetic polymer. The natural bio-based polymer involved synthesis by living organisms such as animal, plants, algae and microorganism reported by Ana Dotan (2014).

Babu et al., (2013) described that the worldwide interest in bio-based polymers has accelerated in recent years due to the desire and need to find non-fossil fuel-based polymers. As indicated by (a) ISI Web of Sciences and (b) Thomas Innovations, there is a tremendous increase in the number of publication citations on bio-based polymers and applications in recent years, as shown in Figure 2.1.

![Figure 2.1: Citation trend of (a) publications and (b) patents on bio-based polymers in recent years (Babu et al., 2013)](image)

Benjamin & Jorg (2008) mentioned that the use of traditional composites from glass, aramid or carbon fiber reinforced plastics have recently concern critically due to increasing of environmental consciousness. Thus the recent research and development efforts have led to new products based natural resources. Some of these are biodegradable polymers like PLA (polylactic acid), cellulose esters, polyhydroxyalkanoates and starch polymer.
2.3 Development of renewable polymer based on sustainable resources

2.3.1 Composition of vegetable oil

Vegetables or plant oils represent a renewable resource that can be used as reliable starting material to access new products with a wide array of structural and functional variations. The ample availability and the relatively low cost make plant oils an industrially attractive raw material for the plastic industry. According to Samarth & Mahanwar (2015), vegetable oil give higher attention of researcher to chemically modify and transform the triglyceride into reactive group via epoxidation process. This is due to functional epoxies group on the structure of epoxidized waste vegetable oil and relatively high oxirane content. Hence, vegetable oil were commonly used as poly(vinyl chloride) plasticizers, lubricants and starting materials to produce polyols, pre-polymer in surface coating formulations and to synthesis of polyurethane.

Vegetable oils are considered to be one of the most important classes of renewable resources because of the wide variety of possibilities for chemical transformations, universal availability, low price and is possible to modify the chemical structure of triglycerides and its derivatives (Miao et al., 2013). The main components of the triglyceride vegetable oils are saturated and unsaturated fatty acids which are important as a fundamental chemical for chemical of polymer synthesis. The term waste vegetable oils includes all vegetable oils such as soybean oil, peanut oil, sunflower oil, linseed oil, coconut oil, cottonseed oil, canola oil, corn oil, safflower oil, walnut oil, castor oil, tung oil, etc. Among the different natural oils, the waste vegetable oils from palm oil is widely explored for bio-polyol synthesis to prevent pollution of waterways and clogging private and municipal drain systems, restaurants and other food preparation.

Vegetable oil has a triglyceride as the molecules contain mostly carbon and hydrogen atoms, with only six oxygen atoms per molecule and has at least one unsaturated fatty acid on the chemical structure. According to Yuan Chan Tu (2008), enzymes or chemicals can be used to modify the unsaturated fatty acid moiety and introduce one or more hydrogen functional groups, enabling it to be converted into polyol. Figure 2.2 shows the chemical structure of fatty acid based on plant oils.
Figure 2. Fatty acid commonly used in polymer chemistry: (i) oleic acid, (ii) inoleic acid, (iii) linolenic acid, (iv) erucic acid, (v) petroselinic acid, (vi) ricinoleic acid, (vii) vernolic acid, (viii) 10-undercenoic acid (Lligadas et al., 2013)

Lu & Larock (2009) reported that the triglycerides differed dramatically in the ratio of the different types of fatty acids present which depends heavily on their origins. The main features of fatty acid are: (1) most fatty acids are a straight chain compound with an even number (8-24) of carbon atoms, (2) the carbon double bonds in most unsaturated fatty acids exhibit a cis configuration, (3) the unsaturated fatty acids with more than two carbon double bonds contain a bi-allylic groups and (4) some special fatty acids containing other functional groups such as hydroxyl or epoxy groups in the vicinity of the double bonds.

United State Department of Agriculture (USDA) mentioned that there are nine major vegetable oils for worldwide productions which are coconut, cottonseed, olive, palm, palm kernel, peanut, rapeseed, soybean, and sunflowerseed. In year 2013-2014, the highest production of vegetable oil was palm oil which conquers 35% from overall vegetable oils production as shown in Figure 2.3. According to Siddique et al., (2010) density of palm oil is 917 kg/m$^3$, soybean (931 kg/m$^3$), sunflower (932 kg/m$^3$) and canola oil (917 kg/m$^3$), respectively. Baroutian et al., (2009) mentioned the molecule weight of virgin palm oil which is 847 g/mol.

![Figure 2.3: Production (million tons and %) of nine major vegetables oil in 2013-2014 (USDA, 2014)]
2.3.2 Renewable monomer based on vegetable oils

Monomer is a single repeating unit of polymer that is covalently bonded into long chains (Smith & Hashemi, 2006; Chang & Cruickshank, 2005). Meanwhile, oil based polyols are often oligomers with a wide distribution of molecular weights and a considerable degree of branching, which affects the viscosity and processing properties of polyurethane foam from them. Precise characterization of the polyol composition and its properties are very important for understanding the synthetic processes as well as for quality control.

Polyols are a component in the production of polyurethanes used in appliances, automotive parts, adhesives, building insulation, furniture, bedding, footwear and packaging. Polyols are traditionally produced from petroleum. The production of polyols from petrochemicals is costly, requires a great deal of energy and has adverse effect on the environment. Henceforth, as an alternative to reduce the usage of petroleum based polyols, bio-polyols are suggested to be obtained from vegetable oils as it is non-petroleum based, renewable, less costly and more eco-friendly. There are several reactive positions of triglyceride vegetable oil which are saturated and unsaturated fatty acids useful in many synthesis transformations to become a new polyol source (Ronda et al., 2011).

The inherent double bonds in triglyceride enable to synthesis of the triglyceride from plants oil by epoxidation, hydroxylation, acrylation, maleunization, hydrogenation, ozonolysis, demerization and methathesis and their derivatives depending on physical properties of aliphatic chain length and distribution of unsaturated (Behr et al., 2008). Among all the synthesis method, the common reaction using intrinsic double bond in plant oil are epoxidation and hydroxylation method.

The utilization of epoxidation oil has become more common over the past few years. For example, epoxidation oil derived from vegetable oils which are considered environmentally friendly. The term epoxidized oil is generally understood to denote oil that is derived from vegetable oils using the epoxidation reaction. Epoxidation oil contains an epoxide group or oxirane ring. The term epoxide may be defined as cyclic ethers which consist of three elements in the epoxide ring. The term oxirane is also usually used to refer to epoxidation according to categorization by International Union of Pure and Applied Chemistry (IUPAC). The epoxidation reaction is an important step in the synthesis of polyols. It plays a key role in contributing to final hydroxyl
groups because epoxide groups will be converted to hydroxyl groups. The chemical structure of epoxide can be in Figure 2.4.

![Chemical structure of epoxide groups](image)

Figure 2.4: Chemical structure of epoxide groups (Purwanto, 2010)

In recent years, different groups have published scientific contributions focused on resins or polymer precursors obtained from vegetable oils and fatty acids. The synthesize monomers based on vegetable oils that could replace petroleum-based monomers such as styrene and divinylbenzene. Meiorin et al., (2015) mentioned that synthesized unsaturated monomers starting from fatty acid and glycidyl methacrylate, which were free radically polymerized with a vinyl ester resin.

Gobin et al., (2015) studies on polyester-type polymer prepared from synthesis of broccoli seed oil and several carboxylic diacids. Meiorin et al., (2015) also reported the high unsaturated tung oil was cationically copolymerization with vegetable derived monomer and replace used a styrene. The synthesized co-monomer is methyl ester of tung oil by transesterification of plant oil with methanol.

### 2.3.3 Waste vegetable oils as renewable monomer feedstock

Waste vegetable based palm oils are most abundant biological sources and important raw materials for the production of bio-based polyurethanes. In polymer industry, waste vegetable oils which represent a major potential source of chemicals have been utilized as an alternative feedstock for bio-monomers (Narine et al., 2007; Rus et al., 2008; Rus et al., 2009). Figure 2.5 shows the composition of waste cooking oil from vegetable resources and the molecular structure is C$_{16}$H$_{32}$O$_{2}$. According to Khalid et al., (2011) the waste cooking oil is subjected as potential raw material for producing biofuel production as well as for polymer feedstock.
Waste vegetable oil which is much less expensive than pure vegetable oil, is a promising alternative to vegetable oil for polymer production. Hanisah et al., (2013) mentioned that the price of waste vegetable oil is RM 1 per 5 kg. Restaurant waste oils and rendered animals fats are less expensive than food-grade canola and soybean oil (Mangesh & Ajay, 2006). The quantity of waste vegetable oil generated per year by any country is huge depending on the use of vegetable oil. An estimate of the potential amount of waste vegetable oil collected in the European Union is 700000-1000000 tonnes/years (Mangesh & Ajay, 2006). A report was published showed that, on an average, 9 pounds of yellow grease per person were produced annually in the United States.

Most of the waste cooking oil from vegetable oil (palm oil) from household and catering premises in Malaysia will eventually ends up in wastewaters (Khalid et al., 2011). Meanwhile, Hanisah et al., (2013) were survey of waste cooking oil produced monthly by frying method at Pahang, Malaysia. Referring to Figure 2.6, the volume of consuming waste cooking oil more than 15 kg with frequency of 12 people contributed from the food business (40 %), housewives (27 %), worker (23 %) and others (10 %). Therefore, waste cooking oil was increasing on year by year.
Moreover, the disposal of waste vegetable oil is problematic due to disposal methods may cause environmental issue. Many developed countries have a set policies that penalize the disposal of waste oil through the water drainage (Dorado et al., 2002). Therefore, Environmental Protection Agency in 1994 released an ordinance under act of oil pollution in which waste vegetable oils could not be exempted from regulation governing the clean-up of oil spills (Kumar & Negi, 2015). The waste vegetable oil must be disposed of safely or be used in a way that is not harmful to human beings. The production of polyurethane foam from waste vegetable oils is one of the better ways to utilize it quality and economically.

2.4 Polyurethane from renewable resources

2.4.1 Polyurethane chemistry

In 1937, professor Otto Bayer and co-workers reported the use of diisocyanate in the polymerization reaction to prepare polyurethane. Polyurethanes (PU) are amongst the most important types of polymers. The term “polyurethane” is given to polymers containing a significant number of urethane groups, regardless of the rest of the molecules present. Generally, polyurethane is obtained from the combination of a polyisocyanate with a reactant consisting of at least two hydroxyl groups in the molecule, known as “polyol”.

For the manufacturer of high molecular weight polyurethanes, two groups of at least bi-functional substances are needed as reactants which are compounds with isocyanate groups and compounds with active hydrogen atoms (polyethers, polyester, etc.). Polyurethane industries are based on the reaction of isocyanate groups with active hydrogen containing compounds. Isocyanates are compounds having one or more highly reactive isocyanate group (-N=O) as refer in Figure 2.7.

These groups will readily react with hydrogen atoms that are attached to atoms that are more electronegative than carbon. Commercial polyurethane products are usually formed by reacting liquid isocyanate components with liquid polyol resin component. In the polyurethanes foaming process, two major reactions take place in the process which is polymerization reaction to form the three dimensional network of
polyurethane structure and gas producing reaction to expand the polyurethane structure from the polymerization reaction.

\[ \text{polyisocyanate} + \text{polyol} \rightarrow \text{polyurethane} \]

Figure 2.7: Synthesis of polyurethane (Lee, 2008)

### 2.4.2 Fundamental principles of polymeric foam formation

The forming process of PU foams consist of three basic stages such as bubble initiation, bubble growth and cell opening (Klempner & Sendijarevic, 2004). Figure 2.8 illustrates the development and formation of a flexible PU foam in an open-mould.

The first stage is bubble initiation was initially introduced by physically bending air into the mixture. This could be done by using a high shear mixing machine or a stirring device that works in a certain rotational speed for entrance of enough bubbles to account for all of the cells present in the PU foam (Latinwo et al., 2010 and Zhang et al., 2011).

The second stage is bubble growth occurs when the gas diffuses and expands, increasing the forming temperature. The gas may originate from sources such as gases involved in water reaction, blowing agents, carbon dioxide and surfactant. The heat generated during the reactions due to exothermic process plays an important role in expansion to form a cellular structure. As the bubble continues to grow, it will begin to enlarge the cell opening to produce polyurethane foam. Combining both foam gas bubbles, or cell, and the polymer phase morphology contributes to determining the properties.
Furthermore, the reaction of polyurethane foam forming occurs between an isocyanate and alcohol as followed by Klempner & Sendijarevic, 2004 as shown in Figure 2.9.

\[
\begin{align*}
\text{Isocyanate} & \quad + \quad \text{Alcohol} \\
\text{R-N=O=O} & \quad \text{R'CH}_2\text{OH} \\
\rightarrow & \quad \text{R-N=C=O}_2\text{CH}_2\text{R'}
\end{align*}
\]

Figure 2.9: Reaction isocyanate and alcohol (Klempner & Sendijarevic, 2004)
During formation of polyurethane, the polyurethane polymer must be expanded or blow by the introduction of bubble and gas. A convenient source of gas is the carbon dioxide, produced in situ from the reaction of an isocyanate group with water is despite in Figure 2.10.

\[
\text{Isocyanate} + \text{Water} \rightarrow \text{Amine} + \text{Carbon dioxide}
\]

Figure 2.10: Reaction of isocyanate and water (Klempner & Sendijarevic, 2004).

### 2.4.3 Polyurethane foam

Polyurethane (PU) foams are versatile engineering materials which find a wide range of applications because of their properties which can be readily tailored by the type and composition of their component. However, the main market for PU foam is in polymeric foam, which are flexible and rigid polyurethane foam (Verjedo et al., 2009). Flexible PU foams are two predominant application forms of PU with coatings, sealants, elastomers, and adhesives being other common forms of applications. PU foam can be produced with open-cell structure to be more flexible or a close cell structure to be a more rigid (Hatchett et al., 2005). Flexible polyurethane foams contributes 47% of the global market share in 2004, followed by 26% of rigid foams and 27% of other applications in CASE, binder, foundry and machinery. Among all PU products, flexible foam is the largest product family and quantity, constituting more than 40% of all polyurethanes. Major applications of flexible polyurethane foam are illustrated in Figure 2.11.

Generally PU foams are one of the major products from urethane material. The characteristic of PU foam can be changed via adjusting the chemical composition of the raw materials, in particular, the polyol and isocyanate in which the PU properties mainly depends on the types of polyol such as functionality and hydroxyl value (Lim et al., 2008). The formation of PU foams follow the same general reaction of isocyanate with polyols and both of which are derived when polymerization reactions occur similar to nearly all polymeric materials (Hatchett et al., 2005).
The preparation of PU foam is divided by two methods such as one-shot method and two-shot method. In the one shot method of fabrication, all materials are put into a mixing cup and mixed homogeneously before they are poured into the mold. The two-shot methods demonstrates that the isocyanate is added to the mixture at the second stage. Abdel Hakim et al., (2011) reported that formation of rigid PU foams was synthesized using one-shot method using polyol based from sugar-cane bagasse.

The fabrication of polyurethane foam is basically between the hydroxyl group (polyol) and crosslinker (isocyanate). For the small or laboratory scale production, the flexible PU foams could be made as a simple hand or cup-foam mixes to techniques of box-foaming mixes according to Klempner & Sendijarevic (2004). In this process, the foam is prepared as free-rise bun. It was noted that the production routes from many laboratory scale foam composite fabrication are actually similar (Table 2.1). The differences between all of the previous works were the time decided for components.
mixing and for foams curing. Table 2.1 lists the time consumed at each stage for flexible PU foam composites production.

Table 2.1: Parameters used for flexible foam composites production

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Preparation of Foam</th>
<th>Foam Cured</th>
</tr>
</thead>
</table>
| 2008 | Sant'Anna et al.| i. The polyol and filler were stirred until completed homogenous for 1 minute and added amine, surfactants and water.  
ii. The crosslinker isocyanate was introducing it mixtures and stirred for 6 seconds and after that, the catalyst were added and stirred for 30 seconds. | The foam sample was leaving to cure for 72 hours |
| 2009 | Mello et al.    | i. Mechanical stirred the polyol and PET particles for 15 seconds at room temperature.  
Polyol with PET particles, water, silicone, catalysts, and stannous octoate at 850rpm were again stirred for 1 minute.  
ii. Addition of isocyanate and methylene chloride to mixtures and stirred for 5 seconds. | After the foam development, the foam was demould and left to rest for 24 hours |
| 2009 | Verdejo et al.  | i. A fixed weight of carbon nanotube was mixed with polyol at 2000rpm for 10 minutes using an overhead stirrer equipped with dispersion disc.  
ii. The surfactant, catalyst, distilled water were added to mixtures and mixed at 2000rpm for 1 minute.  
iii. Isocyanate was added and stirred for 15 seconds before foaming occurred. | The foam in mould was transferred into oven at 50°C overnight and demould |
| 2010 | Lantiwo et al.  | i. The mixture of polyol with filler (calcium carbonate) was added to the content of the mixing chamber and stirred for 6 s.  
ii. The surfactant, catalyst and water as the blowing agent were added to the mixture the polyol and filler in the mixing chamber and thoroughly premixed.  
iii. The isocyanate was weighed directly into this mixture and the completed formulation was | After 10 min the foams were removed from the mould and left to cure for at least 7 days |
REFERENCES


Zolkarnaian, N. & Yusof, M. (2007). Quality of Some Fatty acids Produced in Malaysia, Malaysia Palm Oil Board (MPOB), Palm Oil Development 47.