

**PHOTO-DEGRADATION OF RENEWABLE BIOPOLYMER BLENDED
WITH THERMOPLASTIC HIGH DENSITY POLYETHYLENE (HDPE)**

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THERMOPLASTIC HIGH DENSITY POLYETHYLENE (HDPE)

NURULSAIDATULSYIDA BINTI SULONG

A thesis submitted in
fulfilment of the requirement for the award of the
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In the name of ALLAH, Most Gracious, Most Merciful.

This thesis especially dedicated to;

My beloved abah & mak

~Sulong Bin Ali & Zabidah Binti Said~

My beloved husband

~Ahmad Syahrul Hisyam Bin Rosli~

My beloved son & daughter

~Ahmad Danish Durrani Bin Ahmad Syahrul Hisyam~

~Alya' Kamalia Zukrina Binti Ahmad Syahrul Hisyam~

~Ahmad Uwais Alqarnie Bin Ahmad Syahrul Hisyam~

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~ All mysiblings~

~My friends~

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“..A little spark of kindness can put a colossal burst of sunshine into someone's life..”

ABSTRACT

High Density Polyethylene (HDPE) is one type of thermoplastic with various applications but non-biodegradable material while biopolymer (BP) is environmentally friendly and degradable materials. However, BP has poor mechanical characteristics and restrict their capacity for varying in applications. Therefore, in this study, HDPE was blended with BP in liquid and particle form to produce BPL/ BPP. The composition ratio of BP blended with HDPE were 5, 10, 15, 20, 25 and 30% wt/wt of BP. These BP, HDPE, BPL/ BPP with different percentages of loading then were exposed to different UV exposure (250h, 500h, 750h, 1000h, 2000h, and 3000h) to identify the photo-degradation process. The formation of functional group of urethane linkages and other absorption peak was identified by using Fourier Transform Infrared Spectroscopy (FTIR). Norrish I and Norrish II reaction was taking place that produced ketone, amide group and carboxylic acid when increase in UV irradiation exposure that identified the photo-degradation process occurs in BPL/ BPP. By increasing percentages of BP loading, Melt Flow Index (MFI) shows decreasing in results indicate good flowability and improved its processability. Dynamic Mechanical Analysis (DMA) also shows a single peak of T_g indicated miscibility blending of BPL and BPP in all percentages of loading. BPL and BPP show higher tensile stress and hardness results as compared to BP. This is revealed the new blended polymer enhanced the mechanical properties of BP itself. Meanwhile, Scanning Electron Microscope (SEM) of BP shows brittle fracture morphology while HDPE shows ductile fracture and BPL or BPP show ductile to brittle morphological structure due to increasing in percentages of BP loading. Ultimately, BPL_{30-3000h}, spider-web-like structure appeared while for BPP_{30-3000h}, revealed a fine lamellar type of structure. Hence, BPL/ BPP successfully produced, and photo-degradation process occur and having good mechanical properties as compared to single materials itself (BP or HDPE).

ABSTRAK

Polietilena Ketumpatan Tinggi (HDPE) merupakan Plastik Haba dengan pelbagai aplikasi tetapi HDPE adalah bahan tidak biorosot manakala biopolimer (BP) adalah bahan mesra alam dan boleh biorosot. Walau bagaimanapun, BP mempunyai ciri mekanik yang lemah dan mengehadkan keupayaannya untuk aplikasi yang berbeza-beza. Oleh itu, dalam kajian ini, HDPE telah diadun dengan BP dalam bentuk cecair dan zarah untuk menghasilkan BPL/BPP. Nisbah peratusan BP yang diadun dengan HDPE adalah 5, 10, 15, 20, 25 dan 30% wt / wt BP. BP, HDPE, BPL / BPP dengan peratusan adunan yang berbeza kemudiannya didedahkan kepada cahaya UV yang berbeza (250h, 500h, 750h, 1000h, 2000h, dan 3000h), dan untuk mengenal pasti proses fotodegradasi, Spektroskopi Fourier Transform Inframerah (FTIR) telah digunakan. Pembentukan kumpulan berangkap rantaian uretana dan penyerapan rantaian lain juga turut dikenal pasti. Reaksi Norrish I dan Norrish II yang menghasilkan kumpulan *keton*, *carboxylic acid* dan *amide* apabila peningkatan pendedahan kepada cahaya UV dapat mengenal pasti proses fotodegradasi yang telah berlaku di dalam polimer. Selain itu, dengan meningkatkan peratusan BP, Ujian Indeks Leburan (MFI) menunjukkan penurunan keputusan yang mana menunjukkan kebolehaliran dan kebolehan pemprosesan bahan. Ujian Mekanikal Dinamik (DMA) juga menunjukkan hanya satu puncak T_g yang dihasilkan yang mana menunjukkan kebolehlarut-campuran BPL dan BPP. BPL dan BPP menunjukkan hasil tegangan dan kekerasan yang lebih tinggi berbanding dengan BP. Ini menunjukkan bahawa adunan polimer baru meningkatkan sifat mekanik BP itu sendiri. Sementara itu, dari Mikroskop Elektron Pengimbasan (SEM), BP menunjukkan sifat rapuh sementara HDPE menunjukkan sifat mulur dan BPL atau BPP menunjukkan sifat mulur ke rapuh apabila meningkatkan peratusan BP. Selain itu, BPL_{30-3000h}, menunjukkan struktur seperti laba-laba muncul sementara untuk BPP_{30-3000h}, menunjukkan struktur jenis lamellar halus. Secara keseluruhannya, BPL/ BPP telah berjaya dihasilkan, dan

proses fotodegradasi telah berlaku yang mana mempunyai sifat mekanik yang lebih baik berbanding dengan bahan tunggal itu sendiri (BP atau HDPE).



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LIST OF SYMBOLS AND ABBREVIATIONS

PO	-	Palm Oil
BM	-	Bio-monomer
BP	-	Biopolymer
BPL	-	Biopolymer Liquid
BPP	-	Biopolymer Particle
HDPE		High Density Polyethylene
FTIR	-	Fourier Transform Infrared spectrometer
MFI	-	Melt Flow Index
SEM	-	Scanning Electron Microscope
DMA	-	Dynamic Mechanical Analysis
%	-	Percentages
°C	-	Degree Celsius
UV	-	Ultraviolet
E'	-	Storage Modulus
E''	-	Loss Modulus
Tan δ	-	Material Damping
V _e	-	Cross Link Density
BP _{0h}	-	Unexposed BP
BP _{250h}	-	BP exposed to 250h UV
BP _{500h}	-	BP exposed to 500h UV
BP _{750h}	-	BP exposed to 750h UV
BP _{1000h}	-	BP exposed to 1000h UV
BP _{2000h}	-	BP exposed to 2000h UV
BP _{3000h}	-	BP exposed to 3000h UV

HPDE _{0h}	-	Unexposed HDPE
HDPE _{250h}	-	HDPE exposed to 250h UV
HPDE _{500h}	-	HDPE exposed to 500h UV
HPDE _{750h}	-	HDPE exposed to 750h UV
HPDE _{1000h}	-	HDPE exposed to 1000h UV
HPDE _{2000h}	-	HDPE exposed to 2000h UV
HPDE _{3000h}	-	HDPE exposed to 3000h UV
BPL _{5-0h}	-	Unexposed 5% BPL blended with HDPE
BPL _{5-250h}	-	5% BPL blended with HDPE exposed to 250h UV
BPL _{5-500h}	-	5% BPL blended with HDPE exposed to 500h UV
BPL _{5-750h}	-	5% BPL blended with HDPE exposed to 750h UV
BPL _{5-1000h}	-	5% BPL blended with HDPE exposed to 1000h UV
BPL _{5-2000h}	-	5% BPL blended with HDPE exposed to 2000h UV
BPL _{5-3000h}	-	5% BPL blended with HDPE exposed to 3000h UV
BPL _{10-0h}	-	Unexposed 10% BPL blended with HDPE
BPL _{10-250h}	-	10% BPL blended with HDPE exposed to 250h UV
BPL _{10-500h}	-	10% BPP blended with HDPE exposed to 500h UV
BPL _{10-750h}	-	10% BPL blended with HDPE exposed to 750h UV
BPL _{10-1000h}	-	10% BPL blended with HDPE exposed to 1000h UV
BPL _{10-2000h}	-	10% BPL blended with HDPE exposed to 2000h UV
BPL _{10-3000h}	-	10% BPL blended with HDPE exposed to 3000h UV
BPL _{15-0h}	-	Unexposed 15% BPL blended with HDPE
BPL _{15-250h}	-	15% BPL blended with HDPE exposed to 250h UV
BPL _{15-500h}	-	15% BPL blended with HDPE exposed to 500h UV
BPL _{15-750h}	-	15% BPL blended with HDPE exposed to 750h UV
BPL _{15-1000h}	-	15% BPL blended with HDPE exposed to 1000h UV
BPL _{15-2000h}	-	15% BPL blended with HDPE exposed to 2000h UV
BPL _{15-3000h}	-	15% BPL blended with HDPE exposed to 3000h UV
BPL _{20-0h}	-	Unexposed 20% BPL blended with HDPE
BPL _{20-250h}	-	20% BPL blended with HDPE exposed to 250h UV
BPL _{20-500h}	-	20% BPL blended with HDPE exposed to 500h UV
BPL _{20-750h}	-	20% BPL blended with HDPE exposed to 750h UV
BPL _{20-1000h}	-	20% BPL blended with HDPE exposed to 1000h UV

BPL _{20-2000h}	-	20% BPL blended with HDPE exposed to 2000h UV
BPL _{20-3000h}	-	20% BPL blended with HDPE exposed to 3000h UV
BPL _{25-0h}	-	Unexposed 25% BPL blended with HDPE
BPL _{25-250h}	-	25% BPL blended with HDPE exposed to 250h UV
BPL _{25-500h}	-	25% BPL blended with HDPE exposed to 500h UV
BPL _{25-750h}	-	25% BPL blended with HDPE exposed to 750h UV
BPL _{25-1000h}	-	25% BPL blended with HDPE exposed to 1000h UV
BPL _{25-2000h}	-	25% BPL blended with HDPE exposed to 2000h UV
BPL _{25-3000h}	-	25% BPL blended with HDPE exposed to 3000h UV
BPL _{30-0h}	-	Unexposed 30% BPL blended with HDPE
BPL _{30-250h}	-	30% BPL blended with HDPE exposed to 250h UV
BPL _{30-500h}	-	30% BPL blended with HDPE exposed to 500h UV
BPL _{30-750h}	-	30% BPL blended with HDPE exposed to 750h UV
BPL _{30-1000h}	-	30% BPL blended with HDPE exposed to 1000h UV
BPL _{30-2000h}	-	30% BPL blended with HDPE exposed to 2000h UV
BPL _{30-3000h}	-	30% BPL blended with HDPE exposed to 3000h UV
BPP _{5-0h}	-	Unexposed 5% BPP blended with HDPE
BPP _{5-250h}	-	5% BPP blended with HDPE exposed to 250h UV
BPP _{5-500h}	-	5% BPP blended with HDPE exposed to 500h UV
BPP _{5-750h}	-	5% BPP blended with HDPE exposed to 750h UV
BPP _{5-1000h}	-	5% BPP blended with HDPE exposed to 1000h UV
BPP _{5-2000h}	-	5% BPP blended with HDPE exposed to 2000h UV
BPP _{5-3000h}	-	5% BPP blended with HDPE exposed to 3000h UV
BPP _{10-0h}	-	Unexposed 10% BPP blended with HDPE
BPP _{10-250h}	-	10% BPP blended with HDPE exposed to 250h UV
BPP _{10-500h}	-	10% BPP blended with HDPE exposed to 500h UV
BPP _{10-750h}	-	10% BPP blended with HDPE exposed to 750h UV
BPP _{10-1000h}	-	10% BPP blended with HDPE exposed to 1000h UV
BPP _{10-2000h}	-	10% BPP blended with HDPE exposed to 2000h UV
BPP _{10-3000h}	-	10% BPP blended with HDPE exposed to 3000h UV
BPP _{15-0h}	-	Unexposed 15% BPP blended with HDPE
BPP _{15-250h}	-	15% BPP blended with HDPE exposed to 250h UV
BPP _{15-500h}	-	15% BPP blended with HDPE exposed to 500h UV

BPP _{15-750h}	-	15% BPP blended with HDPE exposed to 750h UV
BPP _{15-1000h}	-	15% BPP blended with HDPE exposed to 1000h UV
BPP _{15-2000h}	-	15% BPP blended with HDPE exposed to 2000h UV
BPP _{15-3000h}	-	15% BPP blended with HDPE exposed to 3000h UV
BPP _{20-0h}	-	Unexposed 20% BPP blended with HDPE
BPP _{20-250h}	-	20% BPP blended with HDPE exposed to 250h UV
BPP _{20-500h}	-	20% BPP blended with HDPE exposed to 500h UV
BPP _{20-750h}	-	20% BPP blended with HDPE exposed to 750h UV
BPP _{20-1000h}	-	20% BPP blended with HDPE exposed to 1000h UV
BPP _{20-2000h}	-	20% BPP blended with HDPE exposed to 2000h UV
BPP _{20-3000h}	-	20% BPP blended with HDPE exposed to 3000h UV
BPP _{25-0h}	-	Unexposed 25% BPP blended with HDPE
BPP _{25-250h}	-	25% BPP blended with HDPE exposed to 250h UV
BPP _{25-500h}	-	25% BPP blended with HDPE exposed to 500h UV
BPP _{25-750h}	-	25% BPP blended with HDPE exposed to 750h UV
BPP _{25-1000h}	-	25% BPP blended with HDPE exposed to 1000h UV
BPP _{25-2000h}	-	25% BPP blended with HDPE exposed to 2000h UV
BPP _{25-3000h}	-	25% BPP blended with HDPE exposed to 3000h UV
BPP _{30-0h}	-	Unexposed 30% BPP blended with HDPE
BPP _{30-250h}	-	30% BPP blended with HDPE exposed to 250h UV
BPP _{30-500h}	-	30% BPP blended with HDPE exposed to 500h UV
BPP _{30-750h}	-	30% BPP blended with HDPE exposed to 750h UV
BPP _{30-1000h}	-	30% BPP blended with HDPE exposed to 1000h UV
BPP _{30-2000h}	-	30% BPP blended with HDPE exposed to 2000h UV
BPP _{30-3000h}	-	30% BPP blended with HDPE exposed to 3000h UV

LIST OF APPENDICES

APPENDICES A	-	List of Publications
APPENDICES B	-	Scanning Electron Microscope (SEM)



CHAPTER 1

INTRODUCTION

1.1 General Introduction

Polymers are a group of materials made up of long covalently bonded molecules, which are obtained either from natural or synthetic sources. Largely through engineering efforts, a series of commercially synthetic polymers have been successfully used in many applications in modern society. Synthetic polymers (commonly known as plastic) like polyethylene (PE), polypropylene (PP), nylon, polyester (PS), polytetrafluoroethylene (PTFE), and epoxy are derived from petroleum hydrocarbons. Polymers, in the form of plastics, are used in making articles of daily use, such as knobs, handles, switches, pipes, heart valves, and so on. In fact, they can be found in all sorts of unexpected places (Nagalakshmaiah *et al.*, 2019). Plastic can be divided into two classes, thermoplastics, and thermosetting plastics. Thermoplastics require heat to make them formable and after cooling, retain the shape they were formed into. These materials can be reheated and reformed into new shapes several times without significant change in their properties. Meanwhile, Thermosetting plastics formed into a permanent shape and cured or 'set' by a chemical reaction and cannot be remelted or reformed into another shape but degrade or decompose upon heated to too high temperature. Thus, thermosetting plastic cannot be recycled (Smith & Hashemi, 2006).

An overwhelming percentage of the polymers to make these commodities are synthesized from petroleum sources or natural gas raw materials. These synthetic polymers are, however, often not environmentally friendly because they typically do

not undergo the process of biodegradation and, of course, are dependent on a limited petroleum resource. Reducing the plastics amount in a series of processes or replaced to green materials are possibly stepped to save the environment (Firdaus, 2019). Approximately 140 million tons of synthetic polymers are produced worldwide every year. Since polymers are extremely stable, their degradation cycles in the biosphere are limited (Islam *et al*, 2016). The urgent need of today is to develop polymers that are biodegradable so that they become environmentally friendly.

Biodegradable polymers from renewable resources have attracted much interest in recent years because of its desirable properties of biocompatibility, biodegradability and natural abundance. Several biodegradable polymers of natural and synthetic origin with good biodegradability and biocompatibility have been made recently (Coppola *et al*, 2021).

In Europe, biodegradable polymers were originally developed and introduced to the markets for two main reasons. Firstly, the limited volume of landfill capacity became more and more a threat and secondly, the bad general image of plastics in public called for more environmentally friendly products. While the first issue has largely disappeared from the top of the agendas due to the introduction of plastics recycling schemes and due to newly built incineration plants, the environmental performance is currently the main argument for bio-based polymers, including their biodegradable representatives (Patel *et al.*, 2005).

Degradation of macromolecular chains by the action of microorganisms is called biodegradation (Agarwal, 2020). From the perspective of a polymer engineer, the term “degradation” is most often used to describe processes that lead to a decline of polymer properties. Degradation of plastic polymers can proceed by either abiotic or biotic pathways. Generally abiotic degradation precedes biodegradation, and is initiated thermally, hydrolytically, or by UV-light in the environment (Gewert, Plassmann, & MacLeod, 2015).

Biopolymers are natural polymers that produced by living organisms and are considered environmentally friendly and sustainable materials (Ayeldeen, Negm & Sawwaf, 2016). Biopolymers catches the greater attention in market because they meet the basic requirements of life cycle environmental impact or life cycle assessments for its proper disposal. In comparison to conventional plastics, some bioplastics like polylactic acid or polyhydroxyalkanoates requires few years for degradation but

unfortunately, these bioplastics are of high cost. One exceptional way to minimize cost is to blend them with natural biomaterials (Thakur *et al.*, 2018).

According to Jia *et al.*, (2015), polyblends are a product by melt-blending or solvent-blending of two or more polymers. The mechanical or physical properties of polyblends depend on the phase morphology, action between continuous and dispersed phase, and the component ratios. In terms of processing technique, phase morphology relies on the processing technique, including extrusion, injection moulding, and manufacturing conditions, such as temperature and shear force. For real applications, polyblends are mostly made by physical blending of melt processing, which blends various polymers on an extruder, compounder, and mixer.

1.2 Background of Study

Concerns on environmental problems caused using non-degradable petrochemical polymers has caused an increasing interest in degradable polymers especially biopolymers from crop plants. Biopolymers are gradually replacing petrochemical polymers and play a bigger role in both fundamental research and application. This is confirmed by having the number of papers and patents recently published linked to biopolymers. Biopolymers been established as a promising class of materials to replace non-degradable polymers in view of their versatile properties. It is environmentally friendly, biodegradable, biocompatible, and it uses renewable plants resources. Besides, it has some interesting properties such as non-toxicity, safe for oral consumption and has abundant availability etc. Biopolymer has been used in different fields such as packaging, medicine, cosmetics, biofuels, biomedics etc (Ibrahim *et al.*, 2019). Like other polymer from petroleum based, polymer from renewable resources is rarely used by themselves. They always used by blending or compositing with other materials for improving the performance and reducing the price (Yu, 2009).

Biopolymers can be used to substitute non-biodegradable plastics to reduce the environmental impact and petro-dependence. As alternative bio-packaging materials, biopolymers allow the packaging materials to be biodegradable or compostable completely. Biodegradation of biopolymers involves the hydrolytic or enzymatic cleavage of bonds in the polymer. Biodegradation is often defined as an event which

occurs via the action of enzymes and/or chemical decomposition associated with living organisms (bacteria, fungi, etc.). It is worth noting that the other processes like photodegradation, oxidation and hydrolysis may also have impact on the structure and chains of polymers prior to or during biodegradation (Zhong *et al.*, 2020).

Biopolymers have much potential and several advantages, but they possess some drawbacks as well. Despite increasing production capacity, they are still quite expensive compared to commodity polymers and their properties are also often inferior, or at least do not correspond to the expectation of converters or users. Although natural polymers are available in large quantities and are also cheap, their properties are even farther from those of commodity plastics. Consequently, biopolymers must be often modified to meet the expectations of the market (Imre and Pukanszky, 2013).

To utilize their potentials and penetrate new markets, the performance of biopolymers must be increased considerably. Consequently, the modification of these materials is in the focus of scientific research. In contrast to the development of novel polymeric materials and new polymerization routes, blending is a relatively cheap and fast method to tailor the properties of plastics. As a result, this approach may play a crucial role in increasing the competitiveness of biopolymers (Imre and Pukanszky, 2013).

Biopolymer mostly derived from 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 are widely explored for bio-polyol synthesis to prevent pollution of waterways and clogging private and municipal drain systems, restaurants, and other food preparation. But, in this study, original vegetable oil was used to produced biopolymer.

Meanwhile, synthetic polymer such as polyethylene is used widely in industry, agricultures and daily life owing to its relatively low price, and good mechanical and processing properties. In the modern world, dependency on petroleum-based polymers has extensively increased over the years. Synthetic polymers such as polyethylene (PE), polypropylene (PP), nylon, polyester (PS), polytetrafluoroethylene (PTFE), and epoxy which is commonly known as plastic are derived from petroleum hydrocarbons. These polymers are an incredibly versatile group of compounds in fact, they can be found in all sorts of unexpected places. Society uses synthetic polymers due to highly

desirable properties, such as strength, flexibility, resistivity, chemical inertness, and so forth (Nagalakshmaiah *et al.*, 2019).

One of the most common polymers that has been used for industrial and commercial products nowadays is High Density Polyethylene (HDPE). The advantages of the HDPE such as lightweight, ease of manufacture, stronger and tough make it preferable than metals (Roslan, 2013). It is used in numerous applications ranging from plastic grocery bags to heavy duty plastics containers. Moreover, HDPE also widely been used in construction industry for producing pipes and as insulator in electrical appliances. According to Dikobea and Luytc (2017), HDPE are abundant, cheap and can be easily processed. However, the primary drawbacks of this material are that its decay consumes a great deal of time, and this affects the environment as this material will be disposed as waste if it could no longer be used (Roslan, 2013).

Polymer blends can provide materials with extended useful properties beyond the range that can be obtained from single polymer equivalents (Ibrahim & Kadum, 2010). According to Abdelwahab *et al.*, (2012), blending is much easier and faster than copolymerization methods.

Polymer blending is an attractive method for producing new polymer materials; moreover, the properties of polymer blends can be controlled by adjusting their composition ratios. Numerous attempts have been made to enhance the properties of bio-based polymers by polymer blending (Hirai *et al.*, 2019). The goal of blending might be the improvement or tailoring of properties to a certain application, or as it is often described, maximization of the performance of a material. However, the specific, primary motivation of blending could be much more diverse. Some example advantages of blending such as cost reduction, the improvement of mechanical properties generally, and impact resistance particularly or the decrease of sensitivity to water are all common aims (Imre and Pukanszky, 2013).

The reasoning behind the blending of a biodegradable polymer with polyethylene is that the biodegradable polymer if present in sufficient quantity will be consumed by micro-organisms in the waste disposal environment leading to the disintegration of the plastic or the film containing the remaining inert component (Reddy, 2008). This concept has led to the development of biopolymer and HDPE blends. One of the possibilities of polymer degradation could be exposed to ultraviolet (UV) light. The morphology and the mechanical properties of the polymer changes

when subjected to UV radiations from the sun, which cause the photodegradation of the polymer because of the chain scission or chemical cross-linking.

Synthesis of bio-monomer is started with the preparation of catalyst to generate the epoxides from the unsaturated fatty compounds of the original vegetable oil. The condensation process comprises of acid-catalysed ring-opening of the epoxides to form polyols. The curing process involves addition of cross-linking agent which allows the polyol group to form (Rus, M. A. Z., 2010). High crosslinked polyol name as Biopolymer (BP) was blended with HDPE named as BPL and BPP at different percentages of loading, also pure HDPE and Biopolymer (BP) were produced to determine the physical and mechanical properties to determine the degradation process upon UV exposure.

1.3 Problem Statement

Commonly known that thermoplastic and thermosetting polymers were widely used nowadays. One of the samples of thermoplastic is High-density polyethylene (HDPE). HDPE plastic has several applications, including packaging for foods (milk and snacks, for example) and cleaners. It is also used for pipe fittings, trays, and hinges. HDPE plastics are suitable for several manufacturing processes including injection moulding, extrusion moulding and blow moulding. The advantages of the HDPE plastic are resistant to acids, bases, alcohol, and vegetable oils, as well as being impact resistant. It is also resistant to sustained heat of about 110°C. But the disadvantages of this thermoplastic are HDPE is non-biodegradable and can take centuries to decompose.

Furthermore, the high environmental burden caused by the used of non-renewable fossil based petrochemical feedstock in the plastic industry has lead to search for renewable materials such as vegetable oil based alternatives. Recently, the use of renewable resources has attracted the attention of many researchers because of their potential to substitute petrochemical derivatives. By renewable resource is meant agricultural products mainly from principal crops: soybean, oil palm, rapeseed, sunflower, and coconut, where the materials are synthesized by sunlight.

Vegetable 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. Naturally occurring plant oils and fatty acids derived thereof the most important renewable feedstock processed in the chemical industry and in the preparation of biobased functional polymers and polymeric materials.

Therefore, it has given attractive benefits to vegetable oils, unlike the toxic, costly, and non-environmentally friendly feedstocks taken from petroleum. Palm oil is among the most attractive renewable alternatives, and palm oil's inherent biodegradability is also a desirable feature in the context of rising environmental concerns compared to petroleum-based products concerning to minimising production costs and maximising inputs and outputs, such as food supply, water management, recovery of energy and products, and waste treatment. Indonesia, Malaysia, and Thailand being the largest producers of palm oil in ASEAN countries will contribute to a significant field of palm oil industry for the oleochemical market.

The biopolymer produced by using catalyst and monomer converter can be one of the alternatives to the renewable materials. The used of biopolymers, in many applications with a short life cycle of the products such as packaging would be an ecologically affordable alternative for reducing the solid plastics waste based petrochemical feedstock. However, biopolymer usually come from small production with high cost, has poor mechanical characteristics in terms of processability and end use implementation, as the fragility and brittleness during thermoforming that can restrict their capacity for varying applications.

Therefore, by taking the advantages and disadvantages of biopolymer and HDPE is to solve the issue by blending the HDPE polymer with the biopolymer would bring a significant impact to the dwi-matrix system. This is also to reduce the petroleum-based dependency as well as to introduce biobased polymer from origin palm oil. In this research, biopolymer from palm oil in liquid form and particle form was blended with HDPE named as BPL and BPP, also pure HDPE and Biopolymer (BP) were produced to enhance the physical and mechanical properties of BP and to determine the degradation process of blended biopolymer when expose in harsh environment condition such as UV exposure.

1.4 Scope of Study

Virgin Palm Oil (PO) was used to convert into bio-monomer using less than 12 L vegetable oils. The monomer preparations is begin with the catalyst preparation by using catalyst converter and second reaction is the production of monomer by using monomer converter. Crosslinker (4, 4'-Methylene Diphenyl Diisocyanate (MDI)) and toluene as solvent agent was added to produced Biopolymer (BP) and then was physically blended with thermoplastic polymer of HDPE. Different percentages loading of BP such as 5%, 10%, 15%, 20%, 25%, and 30% in two form which is in liquid and solid particle was blended with HDPE. The resultant polymers are namely as BPL and BPP. BP, HDPE, BPL, and BPP were exposed in UV weatherometer at different UV exposure, which is 250h, 500h, 750h, 1000h, 2000h, and 3000h. Physical and mechanical properties also photo mechanism development of BP, HDPE, BPL, and BPP were examined by means of Fourier Transform Infrared (FTIR), Melt Flow Index (MFI), Density Test, Hardness Test, Dynamic Mechanical Analysis (DMA), Tensile Test (UTM machine) and Scanning Electron Microscope (SEM).

1.5 Objectives of this work

- i) To produce biopolymer (BP) from renewable oil that is palm oil via catalyst converter and monomer converter.
- ii) To fabricate BP with HDPE using different form of Liquid and Solid Particle of BP by using blending process.
- iii) To identifying the functional groups of BP, HDPE and blended BP/HDPE (BPL/BPP) by means of Infrared Spectroscopy (FTIR) for unexposed and exposed ultra-violet (UV) irradiation
- iv) To determine the degradation process of UV irradiation exposure and unexposed of BP, HDPE, and blended BP/HDPE (BPL/BPP)
- v) To analysis the physical and mechanical properties of BP, HDPE, and blended BP/ HDPE (BPL/BPP) of UV irradiation exposure.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Introduction

This chapter discusses and reviews previous studies from other researchers on properties of vegetable oils, bio-monomer, biopolymer, thermoplastic polymer and biopolymer blended with thermoplastic and also studies the development of photo mechanism by means of UV exposure for biopolymer, thermoplastic polymer and biopolymer blended with thermoplastic. It helps to provide more information and explanation especially in bio-monomer, biopolymer properties and blended biopolymer properties.

2.2 Vegetable oils

Natural oils can be extracted from plant and animal resources (Adekunle, 2015). According to Lligadas *et al.*, (2013); Ying, (2011); Selaimia, Beghiel & Oumeddour, (2015), the utilization of vegetable oils is currently in the attention of various industries especially in the chemical industry, as they are one of the most important renewable platform chemicals due to their universal availability, low price, inherent biodegradability, and superb environmental credentials such as low ecotoxicity and low toxicity toward humans.

Vegetable oils one of the common resources to produced natural product. It's also one of the most important classes of bio-resources for producing polymeric materials. Soybean, linseed, castor, sunflower, rape seed, and palm oils are some examples of plant oils. Plant oils usually extracted from plant oils while animal oils come from animal fats. Natural oils, which can be derived from both plant and animal sources, are abundant in most parts of the world, making them an ideal alternative to chemical feedstocks (Wool, 2005). According to Ying, (2011), in the chemical industry, vegetable oils have a wide range of applications such as soaps, drying agents, coatings, hydraulic fluids, lubricants, monomers (e.g. polyols and dimer acids), and polymers. While, according to Adekunle, (2015), plant oils are renewable raw materials for a wide variety of industrial products, including coatings, inks, plasticizers, lubricants, and paints. Furthermore, soybean oil, for example, has been used extensively in the food processing industry such as in salad dressings, sandwich spreads, margarine, and mayonnaise and in non-food applications like crayons, paints, and soy candles. Vegetable oil also can be use as biofuels as intended to replace the fuel from petroleum (Selaimia, Beghiel & Oumeddour, 2015); (Ying, 2011).

Efforts are made on a global scale to develop innovative technologies to transform these natural resources into novel monomers and polymers. Some of these technologies have already generated competitive industrial products with properties comparable to conventional petrochemical polymers. Fillers and fibers have also been incorporated into these bio-based polymer matrices to improve the physical and thermal-mechanical properties of the resulting composite materials. The development of multifunctional composite materials facilitates the application of these materials in new areas, e.g., sensors, structural parts, medical device, construction units, flame retardant parts (Zhang *et al.*, 2017).

According to Belgacem & Gandini (2008), in year 2000, 17.4 kg production of oils and fats per year per capita were amounted and it is estimated that these figures grow at a rate of 3.3% per year. There was over 110 million tons of the total worldwide yearly production of these renewable materials in year 2002. Vegetable oils constitute the main fraction of this production which is 80% while the remaining 20% being animal fats. Only 15.6 million tons (around 15%) of these raw materials are used as precursors to the synthesis of new chemical commodities and materials. The rest is used for animal (about 5%) and human consumption (around 80%). The main country involved in oleochemistry located in Asia, because of the climatic suitability for such

agricultural activity which is Malaysia, Indonesia and Philippines being the main producers. Fats from animal biomass are produced mostly in the US and Europe. The production of fats and oils for the four main landmasses were Asia, North America, Europe and South America, which is 44%, 16%, 15% and 14% respective.

Vegetable oils are one of the most important classes of bio-resources for producing polymeric materials. According to Sun (2005), vegetable oil is one type of lipid, stored in an organelle in the form of triglycerides, during oilseed development. A lipid is a molecule with diverse structural groups that are hydrophobic. Lipids contain a large variety of fatty acids pigments, and secondary compounds that are metabolically unrelated to fatty acid metabolism. Different vegetable plant species contain lipids with different fatty acid composition and distribution.

The main components of vegetable oils are triglycerides – esters of glycerol with three fatty acids (Miao *et al.*, 2014; Wool, 2005). Vegetable oils as show in Figure 2.1 are esters formed by glycerine and different fatty acids containing from 8 to 24 carbon atoms and between 0 and 7 carbon-carbon double bonds, depending on the plant type and climatic conditions of growing. The structures of the most common fatty acids found in vegetable oils are provided in Table 2.1. Their fatty acid composition distinguishes the vegetable oils, including the stereochemistry of the double bonds, the degree of unsaturation, and the length of fatty acids (Zhang *et al.*, 2017)

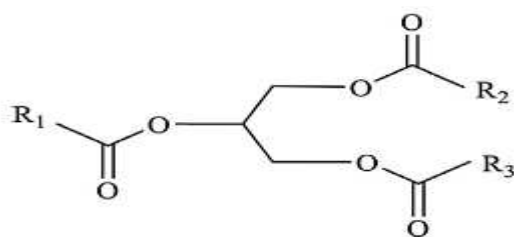






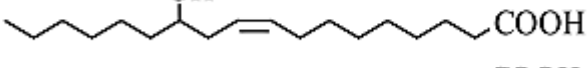




Figure 2.1: Triglyceride structure (R1, R2, and R3 represent fatty acid chains)
(Zhang *et al.*, 2017)

Table 2.1: Common fatty acids composition in vegetable oils (Zhang *et al.*, 2017)

Fatty acids	Formula	Structure
Caprylic	$C_8H_{16}O_2$	
Palmitic	$C_{16}H_{32}O_2$	
Stearic	$C_{18}H_{36}O_2$	
Oleic	$C_{18}H_{34}O_2$	
Linoleic	$C_{18}H_{32}O_2$	
Linolenic	$C_{18}H_{30}O_2$	
Ricinoleic	$C_{18}H_{34}O_3$	
α -Eleostearic	$C_{18}H_{30}O_2$	
Vernolic	$C_{18}H_{32}O_2$	

2.3 Polymer

The word “polymer” means “many parts” (from the Greek word “poly”, meaning “many” and “meros”, meaning “parts”). Polymers are giant molecules with molar masses ranging from thousands to millions of atomic mass units. Polymers are found throughout nature: proteins (silk, collagen, keratin), nucleic acids (DNA, RNA), carbohydrates (glycogen, cellulose, starch), natural rubber (monomer: isoprene) and etc (Schmitz, 2011). While, according to Young & Lovell (2011), polymer is a substance composed of molecules which have long sequences of one or more species of atoms or groups of atoms linked to each other by primary, usually covalent bonds.

According to Painter & Coleman (1997), polymer is very long molecules (macromolecules) that are comprised or built up of smaller unit or monomers. The arrangements of these units, the various types of chains that can be synthesized and the shapes that these chains can blend themselves into, result in a class of materials that are characterized by enormous and intriguing range of properties. According to Kumar & Gupta (2003), polymers are materials of very high molecular weight that are found to have multifarious applications in our modern society. They usually consist of

several structure units bound together by covalent bonds. Polymer are obtained through the chemical reaction of small molecular compound called monomer. For example, polyethylene is formed from monomer called ethylene. To form polymer, monomer either have reactive functional group or double bond (or triple) bonds whose reaction provides the necessary linkage between repeat unit.

The response of a polymer to mechanical forces at elevated temperature is related to its dominant molecule structure. One classification scheme for these materials is according to behaviour with rising temperature. Thermoplastics polymer and thermosetting polymer are two subdivisions. Thermoplastics soften when heated (and eventually liquefy) and harden when cooled- processes that are totally reversible and may be repeated. On a molecular level, as the temperature is raised, secondary bonding forces are diminished (by increased molecular motion) so that the relative movement of adjacent chains is facilitated when a stress is applied. Irreversible degradation results when the temperature of a molten thermoplastic polymer is raised to the point at which molecular vibrations become violent enough to break the primary covalent bonds. In addition, thermoplastics are relatively soft. Most linear polymers and those having some branched structures with flexible chains are thermoplastic. These materials are normally fabricated by the simultaneous application of heat and pressure. Thermosetting polymers are network polymer. They become permanently hard during their formation and do not soften upon heating (Callister, 2005).

According to Zang *et al.* (2017), polymers have taken on a vital role as materials in modern applications in almost every sector of manufacturing, including aerospace, automotive, marine, infrastructure, medical devices, consumer products, and sports equipment due to their tuneable properties, easy processability, high strength/ density ratios, resistance to chemical and physical degradation, and low cost.

Worldwide, the consumption of polymers grows at an annual rate of 5%, with a total annual consumption exceeding 300 million tons. Petrochemical resources are non-renewable and long-term will not provide enough feedstock at economically viable costs. Furthermore, markets are sensitive to disruptive price fluctuations caused by various economic and political factors. Environmental concerns (minimizing air, water, and soil pollution) and the non-degradable nature of most synthetic polymers pose significant challenges for sustainable development. These factors initiated the development of innovative technologies for novel polymeric materials from renewable feedstocks.

According to Islam *et al* (2015), approximately 140 million tons of synthetic polymers are produced worldwide every year while according to Devadas *et al.*, (2021), from PlasticsEurope (2019), these synthetic polymers have an annual production of 359 million tons in 2018 throughout the world. This reserves approximately about 4% of the total global oil production to generate the carbon source energy for the manufacturing process of synthetic polymer and plastic products.

Since polymers are extremely stable, their degradation cycles in the biosphere are limited. In the Western Europe alone, it is estimated that 7.4% of municipal solid wastes are plastic, which are classified as 65% polyethylene/polypropylene, 15% polystyrene, 10% PVC, 5% polyethylene terephthalate and remaining others. Environmental pollution by synthetic polymers, such as waste plastics and water-soluble synthetic polymers in wastewater has been recognized as a major problem (Islam *et al.*, 2015).

While, according to Plastics Insight (2019), polyethylene is one of the most used polymers globally. The production of polyethylene polymer globally was 103 million tons in 2016. The production for high-density polyethylene was 47.5 million tons in 2016. It occupied a share of 46% in total polyethylene production globally. The leading region for production of high-density polyethylene polymer is Asia and Middle-East. In past few years, there is a shift in major production region from North America to Asian and Middle East. This is due to most of the incremental production capacity has been added to this region.

The global production and widespread consumption of polymers have been dramatically increasing from years to years (Bhuyar *et al.*, 2019). Furthermore, according to Haider *et al* (2019), over 250 million tons of commodity polymer annually (mainly polyolefins) are produced worldwide. The polymer materials are strong, durable and very slow to degrade which resulted to become waste. The littering, over-consumption and disposal of polymer have resulted in serious environmental pollution (Zhao, Lv & Ni, 2018). Most of the polymer such as polyethylene (PE), polystyrene (PS) and polypropylene (PP) are majorly plastic waste found in landfills. These polymers are long lasting and show high persistence in the environment, which is seen as an advantage in many applications (such as pipes, aircraft, etc.). However, when they are disposed of in an uncontrolled fashion, they will accumulate in nature for decades as example, a poly (ethylene terephthalate) (PET) bottle has an estimated

life expectancy of 27 to 93 years at 100% relative humidity. These polymers affect the ecosystem and environment with increasing accumulation of plastic waste.

Plastic is a material in which the applications are widely used. The production of plastics always growth faster due to low cost, reusable and lightweight. Plastics is hard to degrade and takes many years to naturally degrade. It is very crucial to know the structure of plastics also the characteristics which change the life span of the material with environmental factors (Moharir and Kumar, 2019). The disposal of plastics waste is usually done by using traditional methods such as landfill, incineration and recycling. The disadvantages of these available methods are the process is not effective and efficient for the disposal of plastic waste (Bhuyar *et al.*, 2019). According to Haider *et al* (2019), the increase of packaging (“convenience packaging”) and other “short-term” uses and the resulting impact of plastic waste on the environment have become heated public issues in recent years. Due to their persistence, plastics accumulate in the environment, are fragmented into smaller pieces (often called “microplastics”) and migrate via rivers to the oceans where they form accumulation zones, so-called “garbage patches”.

According to Folino *et al.*, (2020), from 1950 to 2015, less than 10% of the overall amount of plastic waste that was produced was recycled, while the remaining part was landfilled or released to the environment. In particular, the production of the petroleum derived polymers increases the CO₂ emissions in the atmosphere, thus contributing to the increase of greenhouse gases (GHG). Moreover, the ever-growing plastic waste that is accumulated into the landfills and in the marine environment has a huge impact on the living organisms of these ecosystems. Therefore, the alternatives methods for disposing the plastic waste still be discovered.

2.3.1 Skeletal Structure of Polymer

Polymer is a substance composed of molecules which have long sequences of one or more species of atoms or groups of atoms linked to each other by primary, usually covalent bonds. They have linear skeletal structure which may be represented by chain with two ends while there are also many non-linear skeletal structures as shows in Figure 2.2 below. Cyclic polymer (ring polymer) has no chain ends and show

properties that are quite different to their linear counterparts. Branched polymers have side chains, or branches, of significant length which are bonded to the main chain at branch point (also known as junction points) and are characterized in terms of the number and size of the brunches. Network polymers have three dimensional structures in which each chain is connected to all others by sequence of junction points and other chains. Such polymers are said to be crosslinked and are characterized by their crosslink density, or degree of crosslinking, which is related directly to the number of junctions point per unit volume, branched and network polymers may be formed by polymerization, or can be prepared by linking together (crosslinking) pre-existing chains (Young & Lovell, 2011).

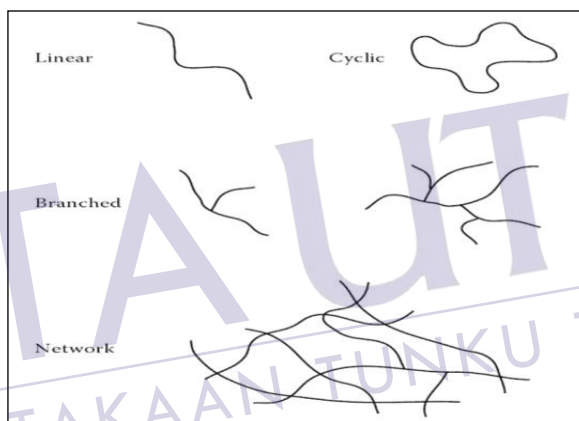


Figure 2.2: Skeletal structure representative of linear, cyclic and non-linear polymers (Young & Lovell, 2011)

2.4 Polyethylene

The general structure of polyethylene is shown in Figure 2.3 below. A polyethylene molecule consists of a long backbone of covalently bonded carbon atoms, to each of which is attached a pair of hydrogen atoms. The chemical formula of this structure is $C_n H_{2n}$. There are numerous variants on this basic structure that fall under the general umbrella of polyethylene. Modifications to the general structure include short and long chain branches, crosslinking, and a variety of terminal groups. Branches may consist

of simple hydrocarbon chains or other more complex structures (Peacock & Calhoun, 2006).

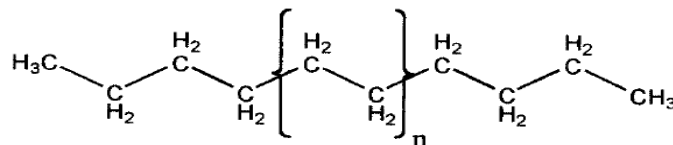


Figure 2.3: Chemical structure of pure polyethylene (Peacock & Calhoun, 2006)

According to Valadez-Gonzalez, Cervantes-Uc & Veleza (1999), polyethylene (PE) is a semicrystalline material whose structure is comprised of three major structured regions: the ordered crystalline region, the disordered (isotropic, interlamellar) amorphous region and the interfacial one. Unlike pure saturated hydrocarbons, commercial grades of PE, are unstable to light due to adventitious impurities (e.g., catalyst residues, hydroperoxides, unsaturation and carbonyl compounds).

According to Amigo *et al.*, (2019), polyethylene (PE) is one of the most widely used commercial polymers due to its good mechanical properties, chemical resistance, and easy processing. PE is used as packaging material due to its high strength, elongation and barrier properties against water-borne organisms responsible for food spoilage. However, despite these good characteristics, PE is a petroleum-based and non-biodegradable material, in opposition to the growing demand for environmentally friendly and sustainable materials such as natural degradable biopolymers.

From another researchers, Grigoriadou *et al.*, (2011), polyethylene (PE) is a widely used as the material in outdoor applications, so its lifetime is determined by various environmental factors as solar radiation, temperature, thermal cycling, humidity, weather, pollutants, but most importantly by ultra-violet (UV) radiation. The most damaging region of wavelengths is between 280 nm and 315 nm. The UV degradation is due to combined effects of photolysis and oxidative reactions. High density polyethylene (HDPE) is the most crystalline of the commercial PEs.

According to Martinez-Romo *et al.*, (2015), polyethylene has a simple and semicrystalline molecular structure, high molecular weight but does not easily degrade

in the natural environment because it does not absorb UV radiation, however, the presence of impurities like catalyst remnants, plasticizers, and antioxidants can induce the PE to absorb UV-B radiation. These properties that make plastics the material of choice for many applications, particularly for single use packaging, together with an increase in usage have also created disposal problems at the end of the useful life of these products. The principal classes of polyethylene are illustrated schematically in Figure 2.4 and different types of polyethylene as shown in Table 2.2 below. Synthetic plastics are widely used in packing of products such as pharmaceuticals, food, cosmetics, chemicals, and detergents. The most widely used plastics in packing are PE (LDPE, HDPE, MDPE, and LLDPE), PP, PS, PVC, PU, PET, polybutylene terephthalate, nylons, and so on. Commonly used synthetic plastic and its applications are listed in Table 2.3 (Rajendran *et al*, 2015).

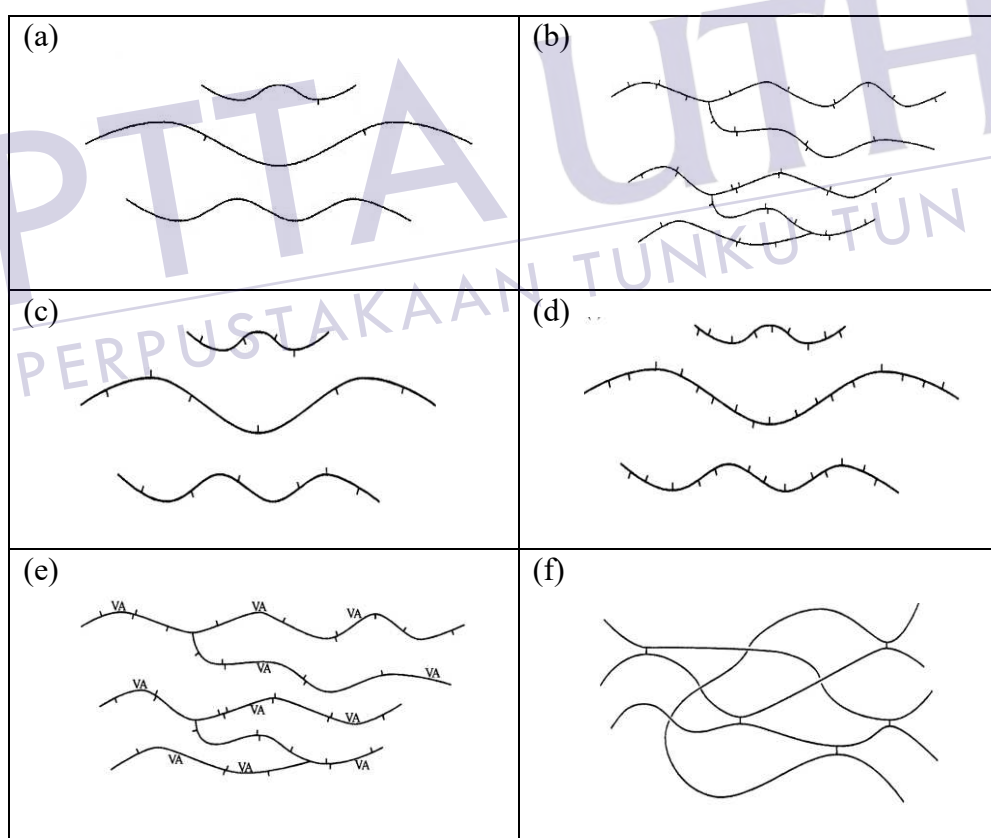



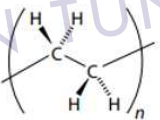

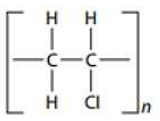

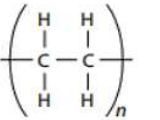

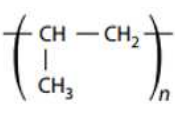

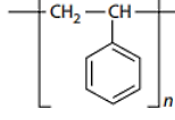

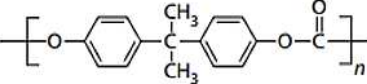


Figure 2.4: Schematic representations of the different classes of polyethylene. (a) High density polyethylene; (b) low density polyethylene; (c) linear low-density polyethylene; (d) very low density polyethylene; (e) ethylene-vinyl acetate copolymer; (f) cross-linked polyethylene (Peacock, A.J. 2000)

Table 2.2: Different types of polyethylene (Visakh & Luftl, 2016)

Type	Abbreviation	Major Characteristics
Ultrahigh molecular weight PE	UHMWPE or PE-UHMW	Outstanding toughness, wear, cut, and excellent chemical resistance
High-density PE	HDPE or PE-HD	Density 0.940-0.970 g/cm ³ low degree of branching
Medium-density PE	MDPE or PE-LD	Density 0.926-0.940 g/cm ³ good shock and drop resistance
Low-density PE	LDPE or PE-LLD	Density 0.910-0.940 g/cm ³ high degree of short-and long-chain branching
Linear low-density PE	LLDPE or PE-LLD	Density 0.915-0.925 g/cm ³ linear polymer with a lot of short branches obtained by copolymerization of ethene and short-chain(C4-C8) alkenes
Very low-density PE	VLDPE or PE-VLD	Density 0.880-0.915 g/cm ³ , Linear polymer with short branches
Crosslinked PE	XPE or PE-X	MDPE or HDPE with significant amount of crosslink bonds that improve, among others, the temperature and chemical resistance

Table 2.3: Commonly Used Synthetic Plastics and Its Applications (Rajendran *et al*, 2015)

Plastic	Symbol	Structure	Applications
Polypropylene terephthalate			Soft drink, water and dressing bottles, peanut butter, and jam bars
High-density polyethylene			Milk, juice and water bottles, trash, and retail bags.
Polyvinyl chloride			Juice bottles, cling films, raincoats, visor, shoe soles, garden hoses, and electricity pipes.
Low-density polyethylene			Frozen food bags, squeezable bottles, flexible container lids.
Polypropylene			Bottles caps, drinking straws, medicine bottles, var batteries, disposable syringes
Polystyrene			Packing materials, laboratory ware, disposable cups, plates, trays, and cutlery.
Others (often-Polycarbonate)			Beverage bottles, baby milk bottles, electronic casing

Polyethylene is classified as a viscoelastic material, with both solid-like and liquid-like properties. With changes in temperature, mechanical behaviour of polyethylene changes due to movement of chains. In Figure 2.5, changes in the storage modulus (E') of polyethylene with changes in temperature are illustrated. At temperature lower than the glass transition temperature (T_g), where only local movement of the polymer backbone and bending of side chains are possible, polyethylene behaves more like a rigid solid with high E' values. At temperature above T_g , larger scale chain movements in the amorphous phase result in polyethylene taking on more liquid-like behaviour and the E' value decreases. At the melting temperature (T_m), crystalline lamellae inside the polyethylene matrix start to melt, large scale chain slippage occurs and the E' value dramatically decreases. At temperature higher than the T_m , polyethylene loses its structural integrity and becomes a viscous melt.

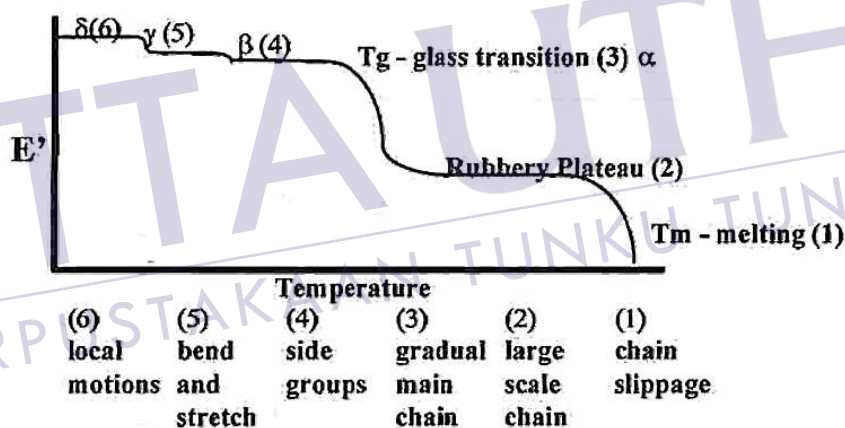


Figure 2.5: Thermal transition stages of polyethylene (Cheng, 2008)

2.4.1 High Density Polyethylene (HDPE)

Polyethylene (PE) is a semicrystalline thermoplastic and is the most widely produced polymer in the world, making it an important commodity material. It also serves as a model thermoplastic system within the polyolefin family because of its simple structure, which is based on ethylene ($\text{CH}_2\text{-CH}_2$) repeat units with varying degrees of crosslinking and branching. One of the various types of PE is high-density

polyethylene (HDPE). HDPE is a linear form with low levels of branching, and consequently a higher density and degree of crystallinity.

HDPE is commonly utilized for its high ductility, toughness, and chemical resistance, for instance in geomembranes, pipelines, and plastic lumber. These and other applications are often outdoors, in which case HDPE would be exposed to varying levels and cyclic variations of temperature, irradiance, and humidity, each of which drives polymer degradation and aging. HDPE exhibits a high chemical resistance. Its high crystallinity and low permeability to most chemicals reduce the reactivity of the solid polymer (Carne, 2009).

Meanwhile, the term plastic lumber applies to products made primarily from plastic (with or without additives), with a rectangular cross-section and size typical of wood products used for building. However, plastic lumber products can also exhibit a circular cross-section, as well as other shapes, with applications such as furniture and farming, among others. Most plastic lumber products on the market are made from polyethylene, particularly high-density polyethylene (HDPE), but can be obtained using polymers, such as polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC), or mixtures of different plastic wastes. Additionally, fillers and additives, such as natural fibers, sawdust, mineral fillers and glass fiber, can be added to plastic lumber formulations (Santos *et al*, 2018).

High density polyethylene (HDPE) is chemically the closest in structure to pure polyethylene. It consists primarily of unbranched molecules with very few flaws to mar its linearity. The general form of high-density polyethylene is shown in Figure 2.4 (a). With an extremely low level of defects to hinder organization, a high degree of crystallinity can be achieved, resulting in resins that have a high density (relative to other types of polyethylene). High density polyethylene resins typically have densities falling in the range of approximately 0.94–0.97 g/cm³.

One of important mechanical properties when describing a polymer is tensile strength. Tensile strength refers to how much pressure a piece of material can withstand before breaking or ripping into two parts. The tensile strength of HDPE is commonly between 3,000 and 3,500 pounds per square inch (psi), which is about 20 to 24 MPa in SI unit. This also allows it to deal with the transportation of high-pressure substances and be easily manufactured into shapes without risk of damaging the materials structure (Roslan, 2013).

Due to its very low level of branching, high density polyethylene is sometimes referred to as linear polyethylene (LPE) (Peacock, 2000). Some of general properties of HDPE can be seen in Table 2.4 while physical and chemical properties of HDPE show in Table 2.5 below.

Table 2.4: The general properties of HDPE (Roslan, 2013)

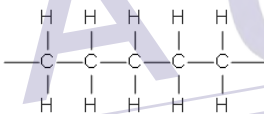
Property	High Density Polyethylene (HDPE)
Melting Point	~ 135°C
Crystallinity	Highly crystalline (>90% crystalline). Contains less than 1 side chain per 200 carbon atoms in the main chain leading to long linear chains that result in regular packing and high crystallinity
Flexibility	More rigid than LDPE due to higher crystallinity
Strength	Strong because of regular packing of polymer chains
Heat Resistance	Useful above 100°C
Transparency	Less transparent than LDPE because it is more crystalline
Density	0.95-0.97 g/cm ³ higher density than LDPE
Chemical Properties	Chemically inert
Schematic diagram	
Uses	Freezer bags, water pipes, wire and cable insulation, extrusion coating

Table 2.5: Physical and chemical properties of HDPE (Kusuktham & Teeranachaideekul, 2014)

Physical description	Properties or value
Melting point	110-140°C
Specific gravity	0.9-1.0
Density	0.9-1.0 g/cm ³
Volatile matter (wt)	< 0.1%
Water absorption (wt)	< 0.05%
Melt flow index	6 g/10 min (2.16 kg at 190°C) or 17.5 g/10 min (5 kg/ 190° C)

According to Graczyk & Ganczewski (2018), as refer to data of the Association of Plastics Manufacturers 'Plastics Europe', global production of plastics (including polyolefin) totalled at 335 million tons in 2016, which means, 4% increase compared to 2015. It must be noticed, that in the years 2011 to 2016 the production of plastics increased by 20%. High demand for plastics reflects their universal character but also high demand for the material among manufacturers.

The most common polymer that has been used for industrial and commercial products nowadays is high density polyethylene (HDPE). High Density Polyethylene (HDPE) polymer is widely being used nowadays. The advantages of the HDPE such as lightweight, ease of manufacture, stronger and tough make it preferable than metals.

Its reasonable cost and low energy demand for processing make it ideal for many applications as packaging, bottles, films, pipes manufacture etc. Also, HDPE distributes well balanced mechanical properties which make it ideal for industrial applications. Its highly crystalline structure, in comparison to other kinds of polyethylene, results in very high tensile strength. On the other hand, HDPE offers a good barrier for humidity and resistance to abrasion and corrosion, and it presents inertness to the most of chemicals. Additionally, it has light weight and low thermal conductivity (Grigoriadou *et al*, 2011).

However, the main disadvantages about this material are that their decaying consumes much time, and this effects the environment as this material will dispose as wastes if they could no longer being used (Roslan, 2013). Therefore, ways to overcome this problem must be found, which is by blended the HDPE polymer with others polymer or materials to enhance the degradation process.

2.5 Biodegradable polymer

Bioplastics were first manufactured back in the 1950s and re-emerged in the 1980s, but only recently received the necessary attention during the 2000s that their industrial-scale production began (Folino *et al.*, 2020).

According to Niaounakis, (2015), degradable is a broad term applied to polymers or plastics that disintegrate by several processes, including physical disintegration, chemical degradation, and biodegradation by biological mechanisms.

As a result of this definition, a polymer may be degradable but not biodegradable. Biodegradable is a term focused on the functionality of a polymer, 'biodegradability', and it is applied to polymers that will degrade under the action of microorganisms such as molds, fungi, and bacteria within a specific period and environment.

According to the withdrawn standard ASTM D5488-94de1, biodegradable polymer refers to polymer that are capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms that can be measured by standard tests, over specific period of time, reflecting available disposal condition. Biopolymers are sustainable, carbon neutral, and always renewable material because they are made from ever-available agricultural nonfood crops (Ayeldeen, Negm & Sawwaf, 2016).

According to Haider *et al* (2019), in January 2018, the European Union (EU) released its vision for a more sustainable plastics industry to be achieved by the year 2030. Besides promoting plastic recycling, the strategy discusses opportunities and risks of (bio)degradable plastics. Development of biodegradable polymers has already been on the upswing for several years as they promise solutions to existing problem.

The Japan Bioplastic Association (JBPA) defines the term biodegradability as the characteristics of material that can be microbiologically degraded to the final products of carbon dioxide and water, which in turn are recycles in nature. Biodegradable should be distinguished from disintegration, which simply means the materials is broken into small and separated pieces. Biodegradability of plastic is determined by the International Organization for Standardization (ISO) methods and evaluated based upon the preestablished criteria (Niaounakis, 2015).

Bio-based is a term focused on the raw materials basis, and it is applied to polymers derived from renewable resources. Raw materials are defined as renewable if they are replenished by natural procedures at rates comparable or fast than their rate of consumption. In recent years, much attention has been focused on research to replace petroleum-based commodity plastics, in a cost-effective manner, with biodegradable materials offering competitive mechanical properties.

Biopolymers can be largely classified in terms of different segregation criteria. Based on their biodegradability, they are divided into biodegradable and non-biodegradable biopolymers, whereas based on their origin, they can be classified as produced from natural sources and fossil fuels. Similarly, based on the thermal

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