ENVIRONMENTALLY FRIENDLY POLYMERIC PLASTICIZER FOR POLY(VINYL CHLORIDE)

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ENVIRONMENTALLY FRIENDLY POLYMERIC PLASTICIZER FOR POLY(VINYL CHLORIDE)

ABSTRACT

Polymeric plasticizers for poly(vinyl chloride), PVC were synthesized using palm oil as the main raw material. A total of four plasticizers with different average molecular weight were prepared. Chemical structure of the plasticizer was analysed using FTIR (Fourier-transform infrared) and ^{1}H-NMR (proton-nuclear magnetic resonance), while the molecular weights were obtained using the GPC (gel permeation chromatography). Plasticization of PVC was carried out using solvent casting technique with tetrahydrofuran, THF as the mutual solvent. Several tests were conducted to investigate the effect of different molecular weights on the efficiency of the palm oil-based compounds as plasticizers for PVC. The performance of the palm oil-based plasticizer was also compared with two commonly used plasticizers for PVC, diethylhexyl phthalate (DEHP) and acetyl triethyl citrate (ATEC). Some of the tests conducted include thermal stability test using TGA (thermogravimetric analyser), determination of glass transition temperature (T_g) using DSC (differential scanning calorimetry), plasticizer migration and leaching resistance test, morphology study of plasticized PVC films using FESEM (field emission scanning microscope), toxicity test, and tensile test. Owing to the plasticizing effect of the palm oil-based compound, T_g of the plasticized PVC has decreased to an average of 65 °C at 20wt % loading of plasticizer in PVC matrix. As for the thermal stability study, result from the analysis shows that polymeric plasticizer is able to contribute positively to the thermal stability of the PVC. The increase in thermal stability is apparent in higher molecular weight plasticizer. Besides, thermal stability of the plastic is studied using the Kissinger's and Flynn–Wall–Ozawa's approaches, it shows that PVC blended with high molecular weight palm oil-based plasticizer is more thermally stable, evidenced by the increase in the activation energy of decomposition, E_d. The polymeric plasticizer is also able to contribute positively to mechanical properties of the PVC films. From the leaching resistance test, plasticizers with higher molecular weight tend to leach at lower rate compared to those with lower molecular weight. Toxicity test using brine shrimp egg shows encouraging results, where the oil-based plasticizer is considerably less toxic compared to some others of the commercial plasticizers.

Key words: Palm oil; polymeric plasticizer; PVC; migration resistance; molecular weight

PEMPLASTIK POLIMER YANG MESRA ALAM UNTUK POLY(VINIL KLORIDA)

ABSTRAK

Pemplastik polimer untuk poli(vinil klorida), PVC disintesis dengan menggunakan minyak sawit sebagai bahan mentah utama. Sejumlah empat pemplastik yang mempunyai purata berat molekul yang berbeza telah disediakan. Struktur kimia pemplastik telah dianalisis dengan menggunakan FTIR (Fourier-transform infrared) dan ^{1}H-NMR (proton-nuclear magnetic resonance), manakala berat molekul diperoleh dengan menggunakan GPC (gel permeation chromatography). Pemplastikan PVC dijalankan menggunakan kaedah tuangan larut dengan tetrahydrofuran, THF sebagai pelarut utama. Beberapa ujian telah dijalankan untuk mengkaji kesan berat molekul yang berlainan terhadap kecekapan sebatian berasaskan minyak kelapa sawit sebagai pemplastik untuk PVC. Prestasi pemplastik yang berasaskan minyak kelapa sawit juga dibandingkan dengan dua pemplastik yang biasa digunakan untuk PVC, diethylhexyl phthalate (DEHP) dan acetyl triethyl citrate (ATEC). Beberapa ujian yang dijalankan termasuk ujian kestabilan termal menggunakan TGA (thermogravimetric analyser), penentuan suhu peralihan kaca (T_g) dengan menggunakan DSC (differential scanning calorimetry), ujian rintangan larut-lesap, kajian morfologi filem PVC yang menggunakan FESEM (field emission scanning microscope), ujian ketoksikan, dan ujian tegangan. Disebabkan oleh kesan pemplastikan dari sebatian berasaskan minyak kelapa sawit, T_g PVC yang mempunyai agen pemplastik telah menurun kepada purata 65 °C pada 20% berat pemplastik dalam PVC matrik. Bagi kajian kestabilan haba, hasil daripada analisis menunjukkan bahawa polimer yang mempunyai agen pemplastik dapat menyumbang secara positif kepada kestabilan haba PVC. Peningkatan kestabilan terma adalah jelas dalam pemplastik yang mempunyai berat molekul yang lebih tinggi. Selain itu, kestabilan haba plastik yang dikaji menggunakan kaedah Kissinger dan Flynn-Wall-Ozawa telah menunjukkan bahawa PVC yang dicampur dengan pemplastik berasaskan minyak sawit yang mempunyai berat molekul tinggi lebih stabil, dibuktikan oleh peningkatan pengaktifan tenaga penguraian, E_d. Polimer yang mempunyai agen pemplastik juga dapat menyumbang secara positif kepada sifat-sifat mekanikal filem PVC. Dari ujian rintangan larut-lesap, pemplastik dengan berat molekul yang lebih tinggi cenderung keluar daripada matrik pada kadar yang lebih rendah berbanding dengan berat molekul yang lebih rendah. Ujian ketoksikan menggunakan telur udang air laut menunjukkan hasil yang menggalakkan, di mana pemplastik berasaskan minyak kurang toksik berbanding dengan beberapa pemplastik komersil.

Kata kunci: Minyak sawit; pemplastik polimer; PVC; rintangan larut-lesap; berat molekul

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LIST OF SYMBOLS AND ABBREVIATIONS

ATEC	Acetyl triethyl citrate
ASTM	American Society for Testing and Materials
$Ca(OH)_3$	Calcium hydroxide
DEHP	Diethylhexyl phthalate
DINP	Diisononyl phthalate
DSC	Differential scanning calorimetry
E_d	Activation energy of decomposition
FESEM	Field emission scanning microscope
FTIR	Fourier-transform infrared
GPC	Gel permeation chromatography
^{1}H-NMR	Proton-nuclear magnetic resonance
KBr	Potassium bromide
KHP	Potassium phthalate
KOH	Potassium hydroxide
kV	Kilovolt
M_w	Weight average molecular weight
NaCl	Sodium chloride
$NaHCO_3$	Sodium bicarbonate
PA	Phthalic anhydride
Plast-A	Plasticizer A
Plast-B	Plasticizer B
Plast-C	Plasticizer C
Plast-D	Plasticizer D
ppm	Parts per million
Pt	Platinum
PTFE	Polytetrafluoroethylene

PVC	Poly(vinyl chloride)
q	Heating rates
R	Hydrocarbon chain of fatty acids
T_c	Crystallization temperature
T_g	Glass transition temperature
TGA	Thermogravimetric analyser
THF	Tetrahydrofuran
T_m	Melting temperature
T_p	Temperature of peak decomposition
VCM	Vinyl chloride monomer
w/w	Weight per weight

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CHAPTER 1

INTRODUCTION

1.1 Poly(vinyl chloride)

PVC was first discovered in the 19th century. In 1835, the first vinyl chloride monomer (VCM) was discovered by Justus von Liebig and his student Henri Victor Regnault (Paul, 2009). Then, in 1872, a German chemist, Eugen Baumann had successfully synthesized PVC from VCM (Baumann, 1872).

Poly(vinyl chloride) or PVC is a synthetic polymer made of natural resource from 57% chlorine and 43% carbon. The chlorine is derived from the electrolysis of salt water while carbon is derived from oil / gas via ethylene. The synthesis of PVC involved polymerization of the vinyl chloride monomer or known as VCM. Figure 1.1 illustrates the formation of poly(vinyl chloride) (Chanda et al. 2006), and the general properties of neat PVC are shown in following Table 1.1.

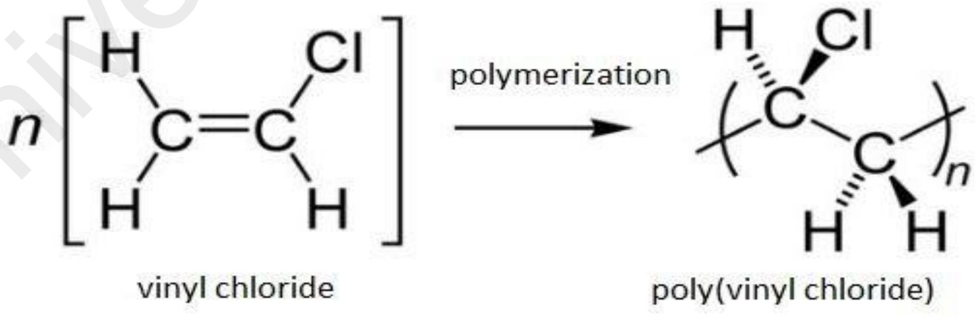


Figure 1.1: Polymerization of PVC

Table 1.1: General properties of PVC (Wilkes et al. 2005)

Properties	**Remarks**
IUPAC name	Poly(1-chloroethene)
Chemical formula	$(C_2H_3Cl)n$
Density (ρ)	1.38 g/cm^3
Melting point (T_m)	212.00 °C
Glass transition temperature (T_g)	83.00 °C
Tensile strength	50.00-80.00 MPa

1.1.1 Applications of poly(vinyl chloride)

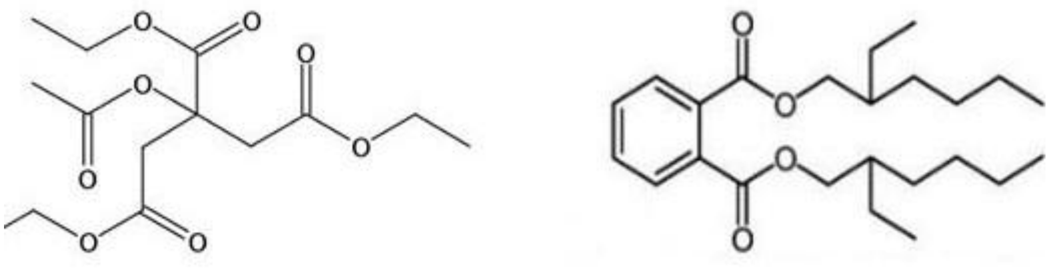
PVC is one of the most versatile thermoplastic polymers. It is a wide ranging purpose synthetic material and is highly valued in the plastic industry. It has been utilized in various applications such as, wire and cable insulation, flooring (Gil et al. 2006), drinking bottles, food packaging (Adam, 2001), children toys (Waskitoajia et al. 2012), automotive, building and construction (Shah et al. 2003). It also has well-known usages in medical sector such as blood catheter, urine and secretion bags, urine catheter, contact lenses as well as gloves (Mihai et al. 2006). PVC by itself can be divided into two classes; unplasticized PVC and plasticized PVC (compounded PVC). Unplasticized PVC is known to be brittle, inflexible and have limited application. The inflexible PVC is mostly employed in construction for pipe, doors or window (Jennifer, 2004). For applications that require flexible PVC, additive material known as a plasticizer is introduced in PVC matrix (Wilkes et al, 2005; John, 2006). According to the Council of the International Union of Pure and Applied Chemistry (IUPAC), plasticizer is defined as a material or substance that incorporated in PVC to enhance its properties such as toughness, flexibility and workability (Richard, 2008). When plasticizer is incorporated into brittle PVC matrix, it will weaken and deteriorate the intermolecular bonds between the polymer molecules, causing the polymer chain becomes more flexible (Jie et al. 2015; Waskitoajia et al. 2012). The following are selection criteria that attribute to be a good plasticizer for PVC; must be compatible with PVC, cost effective, stable, and has high resistance of permanence properties.

1.1.2 Classification of plasticizer

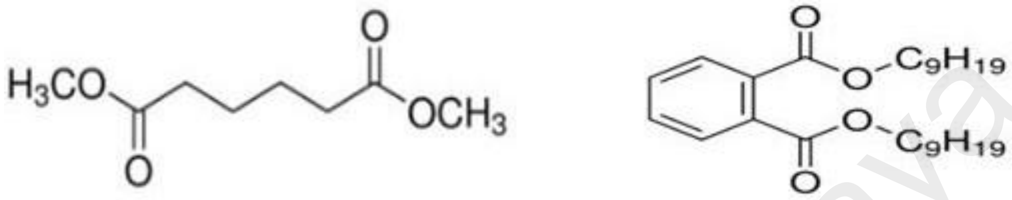
Plasticizer can be classified according to its chemical composition, such as phthalate, terephthalate, aliphatic, epoxies, and trimellitates. Besides, plasticizers can also be categorised according to its molecular weight and structure; monomeric plasticizer and polymeric plasticizer.

1.1.3 Monomeric plasticizer

Some commercially available plasticizers for PVC include esters, phosphate and epoxides (Badra et al. 2008). Phthalate ester which is di-2-(ethylhexyl) phthalate or known as DEHP is commonly used in construction materials and medical devices. Dimethyl adipate is a plasticizer used as solvent for paint stripping and resins, and also for pigment dispersant. Meanwhile, diisononyl phthalate (DINP) is a phthalate used as a plasticizer, and it is made up of isononyl esters of phthalic acid. All plasticizer mentioned above were generally used as monomeric plasticizer for PVC (Jung et al. 2003). Figure 1.2 illustrates the examples of common plasticizers for PVC.



Acetyl triethyl citrate (ATEC) Diethylhexyl phthalate (DEHP)



Dimethyl adipate Diisononyl phthalate (DINP)

Figure 1.2: Common plasticizers for PVC (Alexander et al. 2015)

1.1.2.2 Polymeric plasticizer

Polymeric plasticizer refers to high molecular weight plasticizer which comprised of many repeating units. A common polymeric plasticizer is polyester-based plasticizer, which is usually synthesized by reaction between dibasic carboxylic acid and glycol or a mixture of different dibasic carboxylic acids with one or more glycols. Figure 1.3 shows the general synthesis of acid termination polyester. Unlike monomeric plasticizer, the polymeric plasticizer is reported to have high performance in permanence properties, volatility and chemical extraction.

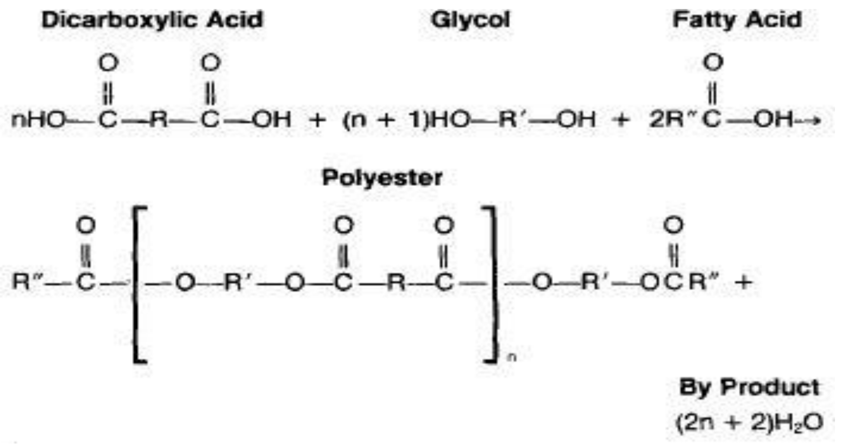


Figure 1.3: Synthesis of polyester

Figure 1.4 below illustrates the interaction between PVC chains and monomeric/ polymeric plasticizer. From the figure 1.4 we can conclude that the polymeric plasticizer has ability to enhance the linking between the PVC chains and tend to prevent the chains from separating (Zahidah et al. 2016).

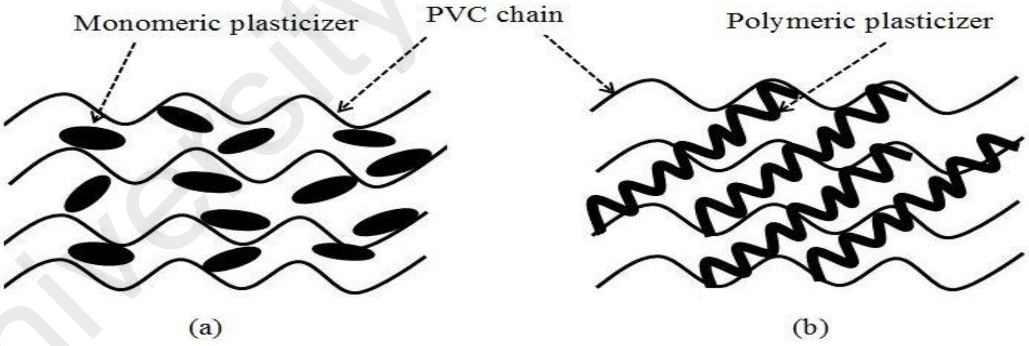


Figure 1.4: Interaction between PVC chains and a) monomeric plasticizer and b) polymeric plasticizer

1.2 Mechanisms of plasticization

There are many different theories that describe the mechanisms of plasticization, including lubricity theory, gel theory, free volume theory and mechanistic or kinetic theory (Paul, 2009).

Based on lubricity theory of plasticization, when system or environment is heated, the molecules of plasticizer will diffuse into polymer matrix and reduce the intermolecular force in polymer chains and the strength of polymer-polymer interactions. The presence of plasticizer also prevents the formation of rigid network and introduces the production of flexible network. Besides that, the incorporation of plasticizer in polymer matrix will cause softness, elongation of polymer, flexibility and extensibility.

According to gel theory, the plasticized polymer is known as an intermediate state between solid and liquid. It is form in three-dimensional network of secondary bonding forces. When the external forces or stresses were applied on plasticized polymer the weak secondary bonding forces between plasticizer and polymer matrix will easily elongate, flex or compress.

Free volume is defined as empty or unoccupied space within a polymer. When the free volume is increased, it will offer more space and free volume for molecule and between polymer chains. The free volume theory of plasticization is related to polymer glass transition temperature (T_g). As plasticizer is added in polymer matrix, the specific volume of polymers is declined when the temperatures declined until the T_g was reached.

Apart from that, kinetic theory of plasticization is based on relationship between resin macromolecules/polymer and plasticizer and plasticizer-plasticizer interactions. At high amount of plasticizer in PVC matrix, plasticizer-plasticizer interactions will dominate, however at low amount of plasticizer, plasticizer-polymer interactions will dominate.

1.3 Effect of common plasticizers to the environment and health

DEHP-plasticized PVC is widely used in the production of kid's rattles, plastic toys, catheters and blood bag (Jung et al. 2003; Michael et al. 2004; Okita et al. 1992; Sunny et al. 2006). Results of several studies found that DEHP plasticizer is not chemically bounded with PVC matrix and only permeate into the polymer chains (Michael et al. 2004; Bhakti et al. 2013). This phenomenon caused the permanence properties of DEHP plasticizer in PVC deteriorated. Thus, DEHP plasticizer will migrate and leach out from the PVC matrix easily and could potentially cause harm especially to our health. DEHP plasticizer has been reported to be carcinogenic laboratory animals such as lab rat (Chris et al. 1999). Besides, during blood transfusion of patient, there are indications of transfer of DEHP plasticizers into the bloodstream. Furthermore, another risk assessment of DEHP plasticizer on human health was identified that it also gives bad effects on kidneys, respiratory, hormones, and fertility (Rosalind et al. 1990; Bornehag et al. 2004). Therefore, DEHP plasticizer is one of the phthalate ester that has been restricted by European Union especially in the production of PVC children's toys (Ted, 2005).

1.4 Vegetable oils as alternative plasticizer

There are concerns and interest to replace and substitute the phthalates plasticizer with those of lower toxicity and leaching rates. Some of the alternative plasticizers include epoxidized soybean oil (Calo’, 2011) and epoxidized sunflower oil (Sun et al. 2017).

In this study, the environmental friendly polymeric plasticizer was produced using palm oil as the main raw. Owing to the fact that our country, since Malaysia is one of the main producers of palm oil in the world, palm oil is very easily accessible in this region. Figure 1.5 shows the stages degradation during thermal decomposition of PVC. One of the advantages of polymeric plasticizer is it has been reported that can increase the thermal stability of PVC.

Besides that, polymeric plasticizer has higher migration resistance than monomeric plasticizer, DEHP. Although, polymeric plasticizer is expected to retain longer in PVC matrix and have strong chain entanglement between them, its high molecular weight could reduce its compatibility with PVC. Therefore, a study on the effect of molecular weight of polymeric palm oil-based plasticizer on its plasticizing efficiency is included in this work.

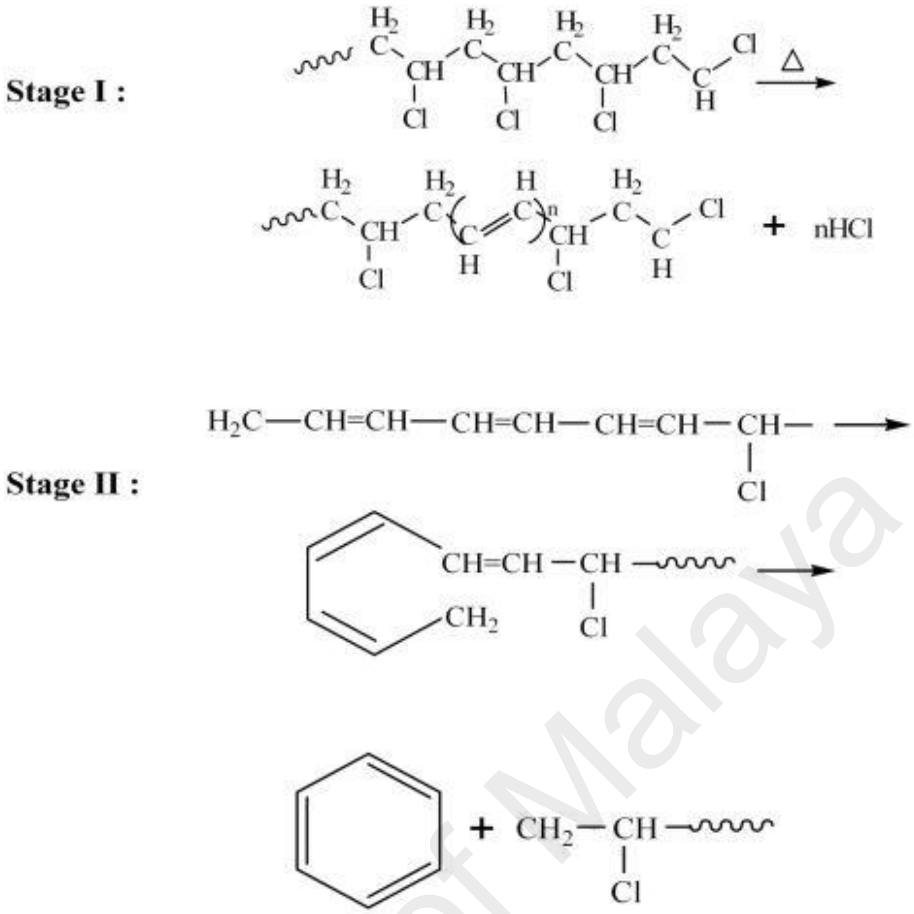


Figure 1.5: Two stages degradation during thermal decomposition of PVC

1.5 Problem statements

PVC is used for various applications, and plasticizer is usually added into PVC matrix to make it flexible. One of the widely used plasticizers is phthalate-based plasticizer such as DEHP. However, there are reports of DEHP leaching out of plastic articles and causes adverse health effect to humans and animals. The problems on migration and leaching of plasticizers can be reduced using polymeric plasticizers. It can retain longer in PVC matrix and has lower tendency to leach out. However, one common concern in using polymeric plasticizer is its limited compatibility with PVC owing to its high molecular weight.

It is therefore important to grasp the understanding on the effect on different molecular weights of polymeric plasticizers on the properties of plasticized PVC film, which includes plasticizing capability and its compatibility, permanence properties, mechanical properties, morphologies and also toxicity. The findings from this study can be used as reference to formulate efficient polymeric plasticizer for PVC.

1.6 Objectives

1. To synthesize environmentally friendly palm oil-based compound with different molecular weights as polymeric plasticizer for PVC
2. To study the effect of molecular weights of palm oil-based polymeric plasticizers on the properties of plasticized PVC film, which includes thermal stability, permanence properties, mechanical properties, morphologies and toxicity.

CHAPTER 2

LITERATURE REVIEW

2.1 Palm oil and its industrial values

Palm oil or scientifically known as *Elaeis guineensis* is recognized and originated from West and Central Africa and in the early 19th century it was introduced in Malaysia. In 1917, Malaysia has been reported to have a commercial scale plantation which first established in Tennamaran Estate in Selangor. By contributing 3.2% to the country's real gross domestic product, Malaysia is recorded to be one of the world's largest producers of palm oil (Basiron, 2007). Malaysia also has produced 18.79 million tonnes of crude palm oil in 2012.

Originally, the palm oil fruit has two types of oils; crude palm oil from the mesocarp and crude palm kernel oil from the kernel. Figure 2.1 shows the ladder stage and cross section of palm oil fruit. Surrounds of fruit is refer to exocarp, surrounds of kernel known as endocarp, and kernel is an endosperm while pulp is refer to endocarp. In this study, the crude palm oil from the mesocarp part has been used as main raw to synthesized the palm oil-based plasticizer.

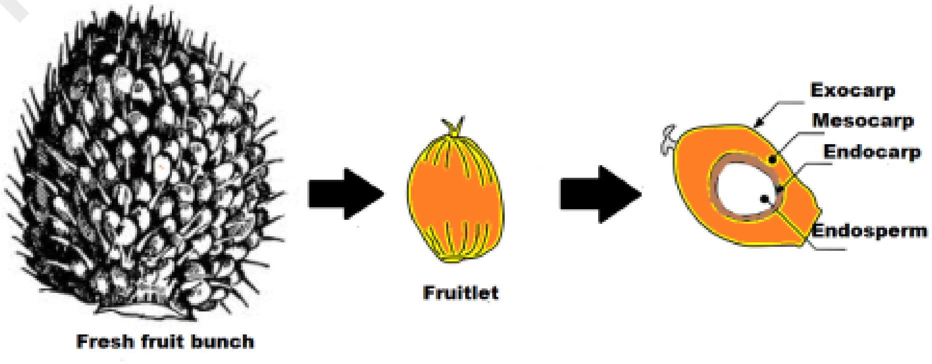


Figure 2.1: Ladder stages of palm oil (Noor et al. 2013)

Palm Oil Research Institute Malaysia (PORIM) has implemented a research study and found that the great potential of palm oil can be used in many applications. Palm oil has wide usage in industries including medical, pharmaceutical, automotive, food manufacturing, furniture, cosmetics, packaging and construction. Other than polyols, the R & D conducted in PORIM also focused on production of palm oil based plasticizer/ polyester, which are more environmentally friendly. The production of palm oil based plasticizer gives more advantage such as lower costs of processing and low capital on raw material (Henderson et al. 2000). Besides that, in order to increase the production and applications of palm oil, the continuous research, innovation and development have been well conducted (Sumathi et al. 2008).

The Table 2.1 displays the fatty acid content of palm oil. It can be clearly seen that the saturated fatty acid is a major constituents of palm oil. The presence of high saturated fatty acid than unsaturated fatty acid allows the final product to be more stable towards oxidation and make it possible to obtain alkyd with lower T_g. The lowered T_g of final product is because of low rate crosslinking during synthesis (Ang, et al. 2016).

Table 2.1: Fatty acid content of palm oil

Types of fatty acid	%
Myristic acid, $C_{14}H_{28}O_2$	1.0%
Palmitic acid, $C_{16}H_{32}O_2$	43.5%
Stearic acid, $C_{18}H_{36}O_2$	4.3%
Oleic acid, $C_{18}H_{34}O_2$	36.6%
Linoleic acid $C_{18}H_{30}O_2$	9.1%
Other/Unknown	5.5%

2.2 Environmentally friendly palm oil-based plasticizer

The global consumption of non-biodegradable plastics and petroleum-based has been increased to 200 million tonnes (Siracusa et al. 2008). Although non-biodegradable petroleum based plastics possess high mechanical properties and are economical, they tend to give bad effects to human health and environment due to waste disposal problems (Farris et al. 2009). The cost of petroleum-derived products has increased when natural resources are decreased, thus the study of environmentally friendly, economical, potential and effective replacement for synthetic or petroleum based plastic has been conducted (Voon et al., 2012).

Currently, the market produces many types of synthetic based plasticizer for varies applications. In the early 1980s, phthalate based plasticizer such as diethylhexyl phthalate DEHP used as predominant plasticizer for PVC has been reported to give adverse health effect and environment. Therefore, nowadays there is an increasing awareness to find alternative plasticizer by using the natural-based plasticizer that has low toxicity, low migration and has excellent compatibility with plastics/ polymer, elastomers, rubbers and resins.

Natural and renewable resources were used as raw materials to produce biodegradable, biopolymer based plastics from vegetable oils. Many works have been done by researchers to synthesize plasticizer for PVC from vegetable oils such as palm oil, sunflower oil, soy bean oil and rapeseed oil (Benaniba et al. 2001; Puyou et al. 2016). Vegetable oils other than renewable resources, are non-toxic, bio-degradable, good heat and light stability, and environmentally friendly. Figure 2.2 shows world production of palm oil and other vegetable oils. From this figure, the palm oil is reported to have the highest utilized vegetable oils compared with soybean, rapeseed, sunflower and others. The utilizing of several vegetable oils as plasticizer for PVC gives advantage in the ability to increase the thermal stability of PVC (Karmalm et al. 2009).

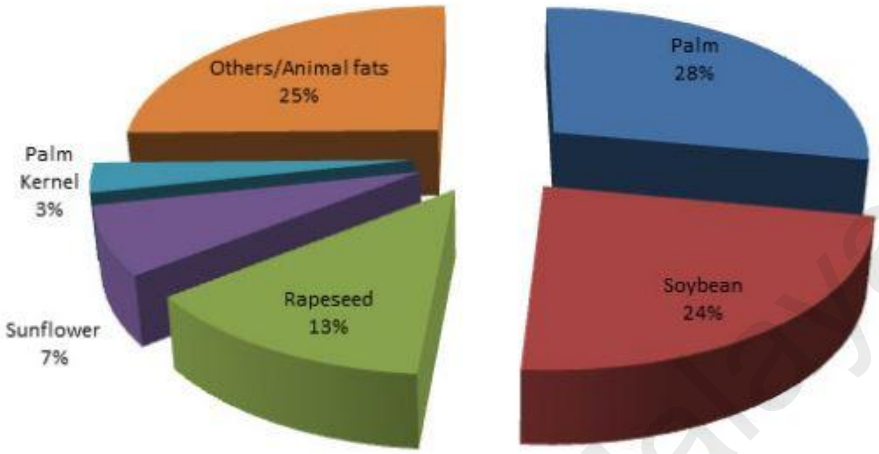


Figure 2.2: World production of palm oil and other vegetable oils (Oil World Annual, 2012)

2.3 Plasticized PVC in medical application and children's products

DEHP is the conventional plasticizer used in medical devices such as dialysis bags, transfusion tubing, IV catheters, nasogastric tubes, blood bags and air tubes. In 1940s, DEHP was first introduced in the PVC blood bags. However, there is indication of DEHP in patient blood during the transfusion. Because of this phenomenon, the concern has been increased for who are at the highest risk of developmental abnormalities especially for newborn in intensive care nursery settings, kidney dialysis patients, premature babies and pregnant women.

Besides that, the uses of diakyl phthalate, diisononyl phthalate (DINP) plasticizer in children's product such as toys, rattles and soft plastic teethers give adverse health effect (Chris et al. 1999). Other than that, phthalates also have been used in pacifiers (Michael et al. 2004). As mentioned above, because these plasticizers are monomeric, they can leach out easily from the PVC matrix and they are not safe to children. When plastic toys are licked and chewed by a child, the plasticizer may be dissolved by the child's saliva and possibly ingested. Therefore, in this study, the polymeric plasticizer derived from palm oil will be synthesized as alternative in order to replace or substitutes the conventional plasticizer used in medical and children's products.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Chemicals and materials

Synthesis of palm oil based plasticizer: Refined, bleached and deodorized palm oil was supplied by Yee Lee Edible Oils Sdn. Bhd. while glycerol was purchased from Friendemann Schmidt Chemical, phthalic anhydride obtained from R & M Chemicals, calcium hydroxide used as catalyst from HmbG Chemicals while methanol and acetic acid were supplied from RCI Labscan Limited.

Characterization of palm oil based plasticizer: Potassium hydroxide, potassium phthalate monobasic and deuterated chloroform solvent for ^{1}H-NMR analysis were purchased from Sigma Aldrich (Steinheim, Germany). Tetrahydrofuran and toluene used for molecular weight analysis were obtained from Friendemann Schmidt Chemical. Brine shrimp eggs was supplied by Ocean Nutrition Europe. Sodium chloride, sodium bicarbonate and p-(1,1,3,3-tetramethylbutyl)-phenyl ether were obtained from Sigma Aldrich (Steinheim, Germany).

Plasticization of PVC: Poly(vinyl chloride) and acetyl triethyl citrate were obtained from Sigma Aldrich (Steinheim, Germany) while di(ethylhexyl) phthalate from MP Biomedicals.

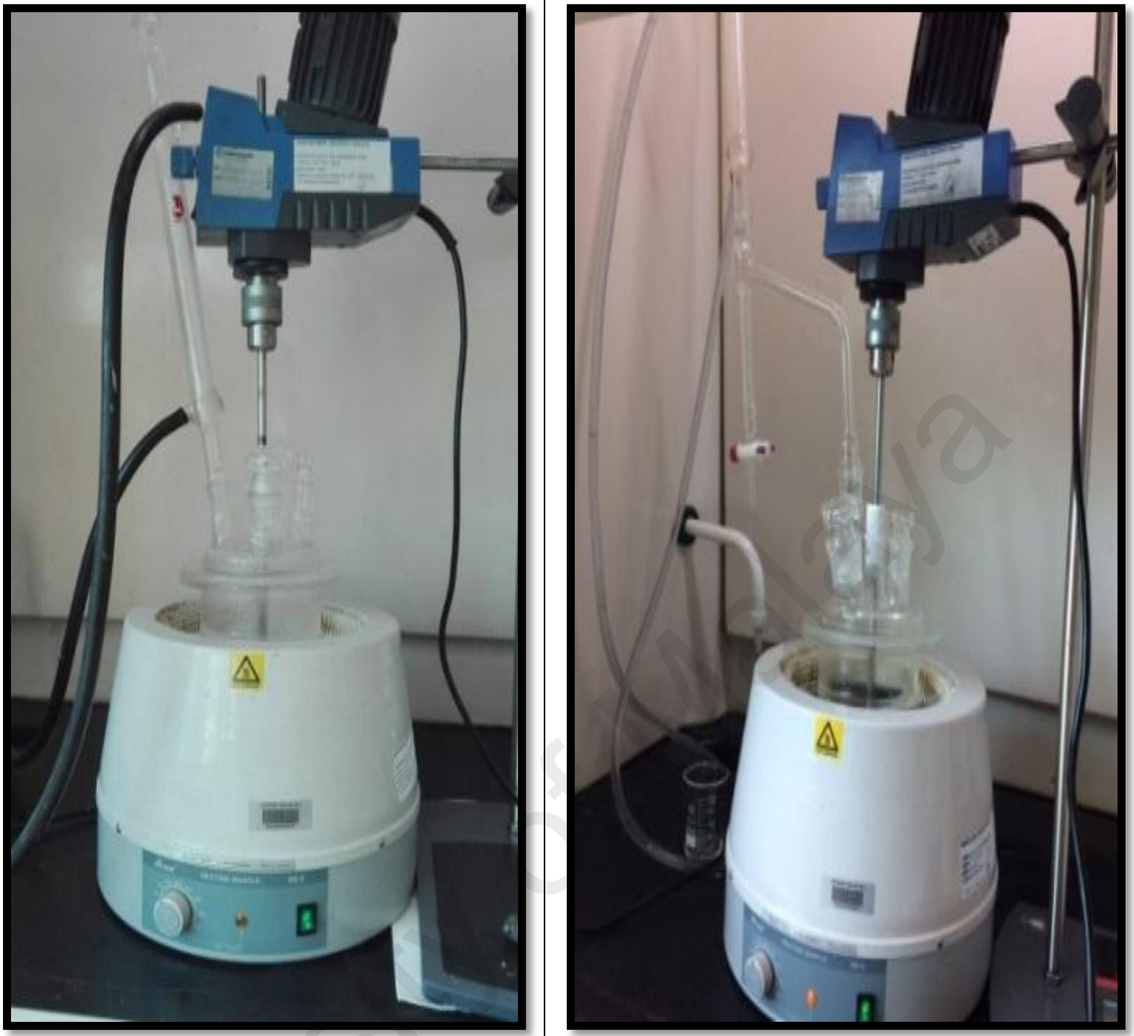
Characterization of plasticized PVC: n-Hexane and ethanol both from RCI Labscan.

3.2 Synthesis of palm oil-based plasticizer

The synthesis of four different molecular weight palm oil-based plasticizers (Plast-A to Plast-D) were produced using the formulation shown in Table 3.1 which involved 2 reactions, alcoholysis and polyesterification. Figure 3.1(i) shows the apparatus setup for reactions to take place which include three-necked round-bottomed reaction vessel equipped with a condenser, a thermometer and a mechanical stirrer placed in a heating mantel. Refined, bleached and deodorised palm oil was mixed with glycerol undergo alcoholysis reaction to produce monoglyceride, diglyceride, and triglyceride at 220 °C in 2 hours. Calcium hydroxide, $Ca(OH)_2$ as catalyst was added in this reaction. The temperature was consequently reduced to 150 °C and the phthalic anhydride was slowly added into the reaction. From this moment, as shown in Figure 3.1(ii) a Dean-Stark apparatus was attached to reaction vessel in order to collect the water produced throughout polyesterification. The temperature then increased back to 220 °C to allow predominant monoglyceride and phthalic anhydride undergoes the reaction. Acetic acid was added only during the synthesis of Plast-C and Plast-D for getting all the palm oil-based plasticizers has the same or comparable hydroxyl value.

Table 3.1: Formulations of palm oil-based compounds

Components	**Compound composition / mol**			
	Plast-A	**Plast-B**	**Plast-C**	**Plast-D**
Palm Oil	0.38	0.36	0.36	0.36
Glycerol	1.81	1.81	1.81	1.81
Phthalic Anhydride	1.94	1.73	1.56	1.38
Acetic Acid	-	-	0.35	0.69
$Ca(OH)_2$ /(x 10^{-3})	3.46	3.29	3.29	3.29



(i) (ii)

Figure 3.1: Apparatus setup for (i) synthesis palm oil- based plasticizer, (ii) polyesterification reaction

3.3 Characterization of palm oil-based plasticizers

The characterizations of palm oil-based compounds include acid value test, nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), viscosity test and toxicity test.

3.3.1 Acid value test

Acid value or acid number is defined as the mass of potassium hydroxide (KOH) in milligrams that is needed to neutralize one gram of chemical substance. In this study, the acid value test of palm-oil based plasticizers was conducted according to ASTM D1639. In order to measure the acid value of reaction mixture from time to time, small amounts of mixture from reaction was dissolved in neutral solvent consist of equal volume of isopropanol and toluene (which was prepared earlier). The mixture was then titrated with standardized potassium hydroxide (KOH) solution and phenolphthalein as indicator was added.

3.3.2 Nuclear magnetic resonance spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy (NMR) is a technique of analytical chemistry used to characterize and determine the organic molecule structure. There are a few types of NMR spectroscopy known; ^{13}C-NMR and ^{1}H-NMR are two of them. The latter has been chosen during the research to identify the type and the number of H atoms in a molecule. Samples for the ^{1}H-NMR analysis were prepared by dissolving the palm oil-based compounds in deuterated chloroform (99.8% $CDCl_3$). ^{1}H-NMR spectra for palm oil-based compounds were recorded in a NMR machine model ECX400MZ-

JEOL. Tetramethylsilane (TMS) is used as an internal standard. The magnetic field is locked by the signal of ^{2}H in deuterated solvent.

3.3.3 Fourier-transform infrared analysis (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a unique analysis to identify unknown substances or characterizes the functional groups in a molecule. In this study, the FTIR analysis was carried out with a FT-IR Spectrometer (Perkin Elmer, Frontier). The samples were prepared by spreading the palm oil-based plasticizers into thin film on a potassium bromide (KBr) cell. The spectra of samples were acquired at a resolution of 4 cm^{-1}, in the range of 400 to 4000cm^{-1} and recorded after 8 scans per sample.

3.3.4 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) analysis was performed to identify the average molecular weight of all four palm oil-based plasticizers. The samples were prepared by using tetrahydrofuran (THF) as a solvent to dissolve the palm oil-based compounds. The samples were then filtered through a 0.45µm polytetrafluoroethylene (PTFE) membrane before the analysis was conducted. The instrument was calibrated with monodispersed polystyrene standards. The number average molecular weights and polydispersity of polystyrene are 3000 g/mol and 1.32, respectively. Each analysis run for 55 minutes.

3.3.5 Viscosity Test

Viscosity is defined as the resistance of fluid to flow which is due to internal friction. The relative viscosity of each palm oil-based plasticizer was identified by conducting a viscosity test. As a viscosity is synonym with molecular weight, the viscosity of the samples can also be used to reflect the relative molecular weight of the palm oil-based plasticizers. The apparatus for viscosity test was setup using an Ubbelohde viscometer which placed in water bath at 30^{o}C. The viscosity test was evaluated by diluting polymeric plasticizers in toluene in order to get a solution with fixed concentration of 40 wt %. The relative viscosity of palm oil-based plasticizer was obtained by measuring the flow time of each sample. Glycerol was used as the main reference (Secur, 2001).

3.3.6 Toxicity Test

Brine shrimp eggs also known as *Artemia Salina* were used to compare the toxicity of polymeric plasticizers and common monomeric plasticizers, DEHP (Naoki, 1974). About 0.1 g of plasticizers was dissolved in 100 ml of 2 % sodium chloride (NaCl) solution to prepare stock solutions. The solution was subsequently adjusted to pH 8 with sodium bicarbonate ($NaHCO_3$). In order to enhance the solubility of plasticizers, 0.02 ml of p-(1,1,3,3-tetramethylbutyl)-phenyl ether (triton- X 100) was added. The 2% NaCl solution was also used to dilute the stock solution. The diluted solution was adjusted back to pH 8 to gain the working solutions consist of five concentrations: 10, 20, 30, 40 and 50 ppm. The samples were prepared by placing about 2 mg of brine shrimp eggs in petri dish, followed by (i) 2% NaCl stock solution (as a control), or (ii) working solutions (as experimental dishes). The temperature of incubator as shown in Figure 3.2 was set at 26 °C and the dishes were placed in the apparatus for 72 hours. Then, the number of eggs hatched was recorded after 3 days.

Figure 3.2 : Incubator for egg hatching

3.4. Plasticization of PVC films

The plasticized PVC film was fabricated using solution casting technique. The PVC and palm oil-based plasticizers (Plast-A to Plast-D) both dissolved in THF separately with designated formulation which can be referred in Table 3.2. Each solution was then blended using the magnetic stirrer continuously in a conical flask surrounded by the water bath. The water condition is at 65^{o}C that monitored by a digital thermometer and the blending was last for 6 hours. The blended solution was then poured into a round petri dish and placed in the fumehood to air-dry for one night. After that, the remaining solvent in the plasticized PVC films was removed by transferring the films in vacuum oven at 70^{o}C in 96 hours. Figure 3.3 shows how exactly the blending process occurred in this research.

Table 3.2: Formulations of plasticized PVC films

Sample	**Composition / wt %**						
	PVC	**Plast-A**	**Plast-B**	**Plast-C**	**Plast-D**	**DEHP**	**ATEC**
PVC-A5	95	5	-	-	-	-	-
PVC-A20	80	20	-	-	-	-	-
PVC-B5	95	-	5	-	-	-	-
PVC-B20	80	-	20	-	-	-	-
PVC-C5	95	-	-	5	-	-	-
PVC-C20	80	-	-	20	-	-	-
PVC-D5	95	-	-	-	5	-	-
PVC-D20	80	-	-	-	20	-	-
PVC-DEHP5	95	-	-	-	-	5	-
PVC-DEHP20	80	-	-	-	-	20	-
PVC-ATEC5	95	-	-	-	-	-	5
PVC-ATEC20	80	-	-	-	-	-	20

Figure 3.3: Setup apparatus for blending

3.4.1 Thermogravimetric analysis (TGA)

Thermal gravimetric analysis or known as thermogravimetric analysis (TGA) is a common technique to investigate the thermal energy. The thermal analysis is described as changes in properties of physical and chemical of materials, which can be measured as a function of time using constant mass loss and temperature or function of increasing temperature using constant heating rate (Coats et al. 2002). In this research, the latter has been chosen to determine thermal stability of plasticized PVC film.

The samples were prepared by cutting the plasticized PVC and unplastisized PVC films into small pieces. The specimens were then transferred in the small ceramic pan. The thermal stability of film was investigated using a thermal gravimetric analyzer (Model: TGA 6, Perkin Elmer). The thermal analysis was performed in the range of temperature (from 50 °C to 900 °C), at flow rate of 20 mL/min in inert atmosphere with different heating rates. Activation energy of decomposition (E_d) is commonly used to study the thermal stability of samples. E_d can be determined using a few degradation models included Kissinger, Coat-Redfern, Flynn-Wall-Ozawa, Friedman and Criado method (Shahla et al. 2012; Ang et al. 2014; Fei et al. 2008; Aboulkas et al. 2008).

The Kissinger equation was used in this thermal analysis to determine E_d. According to this equation, symbol of q is referred to heating rates while T_p defined as temperature of peak decomposition. Different values of q, varies from 10 to 30 ^{o}C/ min were used for each sample throughout analysis. Then, T_p from each analysis was recorded to plot a graph of ln (q/T_p^2) against $1000/T_p$ to get the E_d of the sample. The result of thermal stability of PVC films obtained from the Kissinger equation was compared with another degradation model, Flynn-Wall-Ozawa (Ruowen et al. 2005).

3.4.2 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is commonly used to study thermal transitions behaviour of a polymer, changes between brittle and rubbery phase – glass transition; changes between crystalline and solid phase – crystallization; and changes between crystalline and liquid phase – melting transition. The respective glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) of PVC films can be obtained by DSC graph. However, the glass transition thermal state was focused in this research due to the ability of the plasticizer to reduce the T_g during the thermal transition (Hanpin et al. 2013).

In this analysis, the sample prepared was similar to the above TGA analysis, by cutting the plasticized PVC film into small pieces. Before the analysis was conducted, a pan without lid was weighted and then tared. The sample will be placed in the pan after being weighed around 8 mg. Next, the pan consist of sample will be placed beside an empty reference pan. The DSC unit from TA Instrument, model Q20 is used to perform the analysis. The samples were scanned from 10 °C to 120 °C at the heating rate of 20°C/min under N_2 atmosphere. The T_g was then determined through the peak within the DSC graph.

3.4.3 Permanence properties

In this research, leaching or migration resistance test was performed to investigate the sustainability of the plasticizer within PVC matrix before migrating to the solvent. As the plasticizer does not chemically bounded to the PVC, it will result in loss of certain properties during the migration. Thus, the mechanism of the polar orientation between the plasticizer and solvent will be determined (Jung et al. 2003).

The samples were prepared by cutting the plasticized PVC films into small square shaped. The permanence property of plasticizers in PVC films was examined by soaking each PVC sample (dimension; 1cm x 1cm) in 5mL of n-hexane solvent in a sample vial. The n-hexane is a typical leaching solvent used. The samples were then placed in an oven which heated up to 50 °C to increase the rate of migrations of the plasticizers in the PVC matrix for 7 days. Then, the UV-Vis spectrometer was used to analyze the n-hexane of each PVC specimen after one week left in oven. In order to identify the weight loss of each sample, the weight of samples were recorded before and after the test. The weight loss of sample is occurred due to the migration of plasticizers from the PVC film.

Besides that, to compare the permanence properties of plasticized PVC using n-hexane as solvent, the migration and leaching resistance test were also performed in a more polar solvent, ethanol/water mixture. The ratio applied for ethanol and water was 2:8 by volume respectively.

3.4.4 Tensile test

The tensile test for mechanical properties; tensile strength, percent elongation and elastic modulus of the controlled PVC (unplasticized PVC) as well as other plasticized PVC films were performed. With the reference ASTM D882 which is designed for standard test method for tensile properties of thin plastic sheeting, the tensile test was carried out using a Zwick/ Roell Z030 (Model No. BZ030/ TH25) with 5 kN load cell setting.

Each sample consists of five specimens were prepared by cutting the PVC films into a dimension (10 mm x 100mm) as shown in Figure 3.4 below. The gauge length known as the length of test section was set at 50 mm. Micrometre screw gauge was used to measure the thickness of specimens. Each specimen was tested with same crosshead speed of 50mm/min. The masking tape was used to cover the grip section of specimens in order to improve the gripping of the sample and also to prevent a slippage when it was pulled by the tensile machine.

The result of tensile strength was calculated by dividing the load with cross sectional area of tensile sample, while the value of percent elongation was calculated by dividing the elongation of rupture with the initial gauge length and multiplied by 100. The elastic modulus or known as Young modulus for each PVC film specimen is a tensile stress over tensile strain. The information of these mechanical properties are recorded and obtained from chart of plotted stress-strain curve.

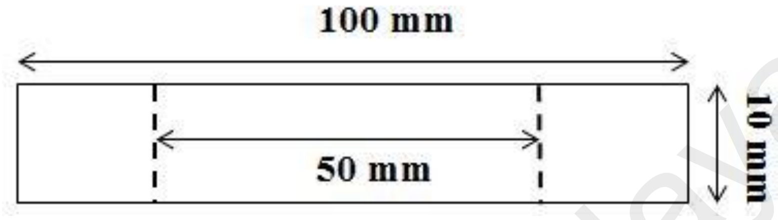


Figure 3.4: Dimension of test specimen

3.4.5 Field emission scanning electron microscope (FESEM)

The morphology property of plasticized film was examined by field emission scanning electron microscope (FESEM) analysis. Before each analysis was conducted, the prepared specimen was coated with a platinum (Pt) layer under vacuum atmosphere to prevent sample charging under the electron beam. The surface images of PVC plasticized by different molecular-weight plasticizer were captured using a JEOL JSM-7600F (JEOL, Peabody, MA, USA) at an electron acceleration voltage of 5kV.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Palm oil-based plasticizer

4.1.1 Observation and Appearances

Table 4.1 reveals the observation, appearance and several properties of the environmentally friendly palm oil-based plasticizer. According to the result from GPC analysis, the weight average molecular weight for Plast-A is 9560 g/mol while Plast-B 4787 g/mol, followed by Plast-C and Plast-D with weight average molecular weight of 4663 g/mol and 2279 g/mol, respectively. It can be clearly seen that Plast-A has higher molecular weight than Plast-B, Plast-C and Plast-D. As the viscosity of the palm oil-based plasticizer can be applied to reflect the relative molecular weight of the plasticizers, Plast-A which has the highest molecular weight, showed the highest relative viscosity, while Plast-D the lowest. Note that the viscosity of Plast-C and Plast-B differ quite significantly despite the small difference in molecular weight due to the difference in the formulations of the plasticizers. Plast-C was formulated with a specified amount of monofunctional acetic acid, while Plast-B was formulated with bifunctional phthalic anhydride as the source of -COOH. Density for all polymeric plasticizer also was recorded, for Plast-A was 1516 kg/m3 and for Plast-B, Plast-C and Plast-D were 1124 kg/m3, 1122 kg/m3 and 1061 kg/m3 respectively. From the acid number test, Plast-A recorded 24.1, Plast-B is 25.6 and Plast-C is 25.1 while Plast-D is 27.0. The final acid value of all this four polymeric plasticizers is similar, an indication that comparable extent of reaction has taken place in the synthesis of the four compounds.

Table 4.1: Properties of palm oil-based and common plasticizers

Plasticizer (Plast-)	Weight average molecular weight, M_w (g/mol)	PDI	Relative viscosity	Observation and appearance
A	9560	4.59	10.2	Dark brown Non-flowable
B	4787	1.42	7.48	Dark brown Slightly flowable
C	4663	1.45	5.44	Dark brown Slightly flowable
D	2279	1.93	4.35	Dark brown Viscous but flowable

4.1.2 Fourier transform infrared analysis (FTIR)

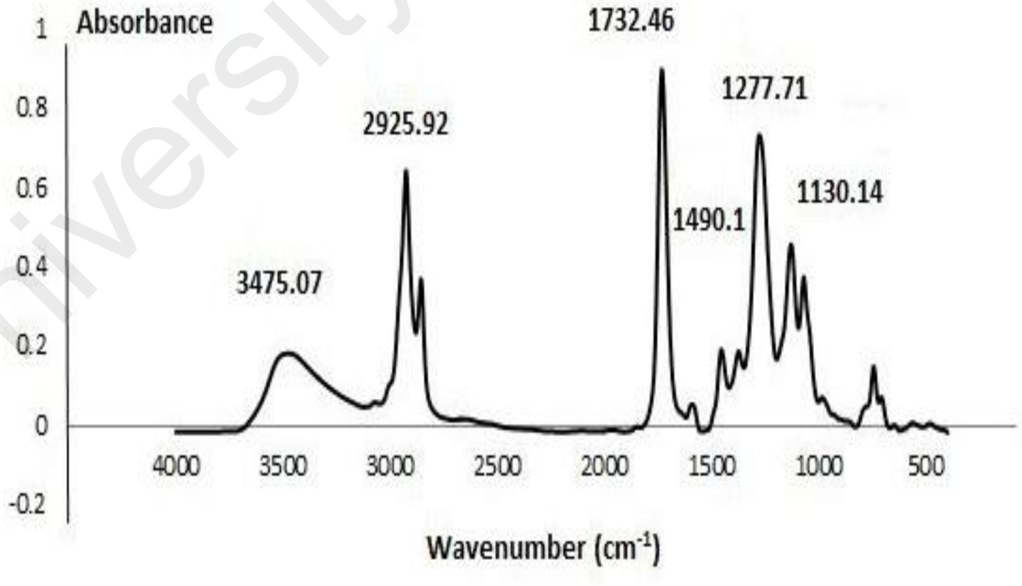


Figure 4.1: FTIR spectra for PLAST-D

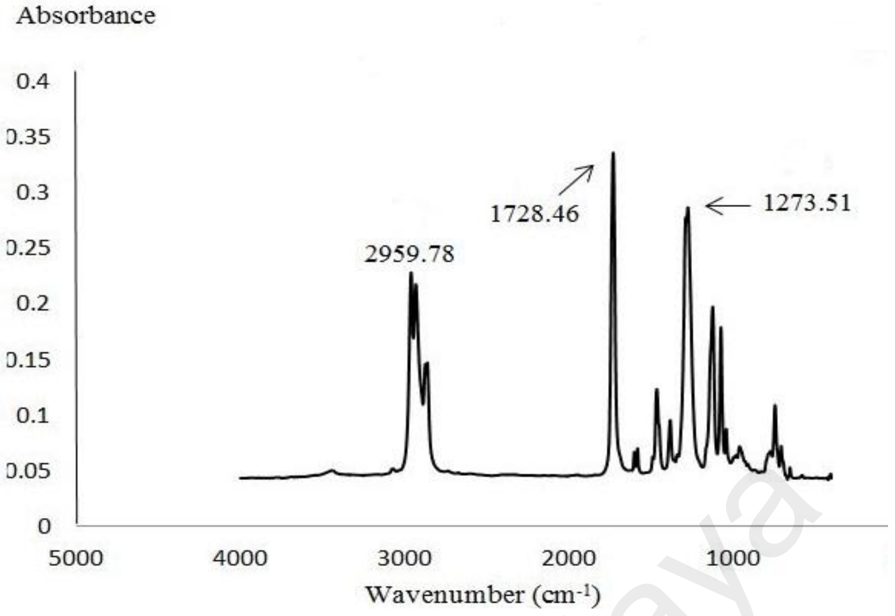


Figure 4.2: FTIR spectra of DEHP plasticizer

The FTIR spectra of palm oil-based plasticizer and DEHP plasticizer are shown in Figure 4.1 and 4.2, respectively. The spectra showed peaks 3475 cm^{-1} which indicated the –OH group, while peaks at 1732 cm^{-1} and 1728 cm^{-1} displayed the -C=O stretching of ester, and -C-O- stretching at 1277 and 1130 cm^{-1}. The spectra of other polymeric plasticizers are not shown as they are similar to each other.

4.1.3 Nuclear magnetic resonance (NMR)

^{1}H-NMR spectrum in Figure 4.3 displays peak at 7.5 ppm and 7.7 ppm which indicated the aromatic proton from incorporated PA. The peak at 4.4 ppm showed methylene protons of glycerol, -OC$\boldsymbol{H_2}$- from ester linkage (George et al. 1986; Reimmel et al. 1994 & Puyou et al. 2016), while 5.3 ppm is attributed resonance of vinyl protons, -CH=C$\boldsymbol{H_2}$ of unsaturated fatty acids, and peaks at 2.0 and 2.3 ppm are from -C=C-C$\boldsymbol{H_2}$- and -OOC-C$\boldsymbol{H_2}$- respectively. Meanwhile, 0.9 to 1.4 ppm are the peaks from the resonance of protons from the hydrocarbon chain of fatty acids.

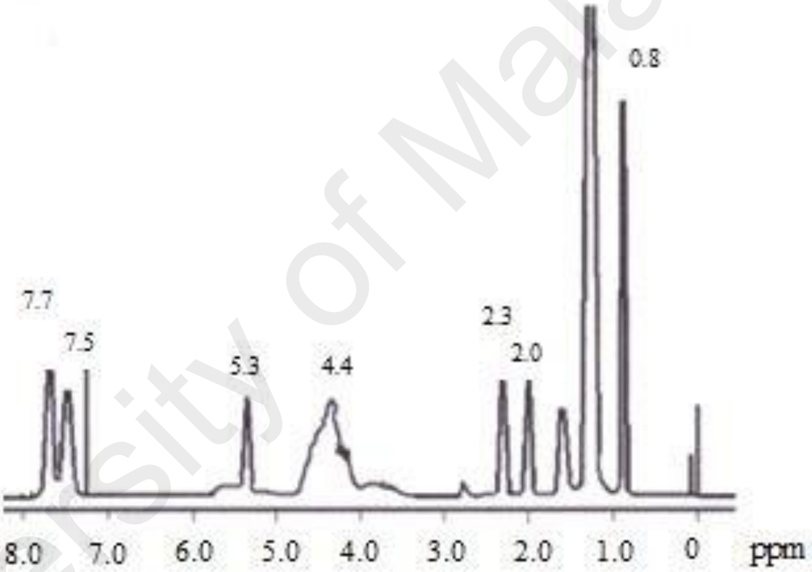


Figure 4.3: NMR spectra of polymeric plasticizer

4.1.4 Chemical structure of plasticizer

Figure 4.4 reveals the chemical structure of plasticizer interpreted from the FTIR and NMR analyses. It can be clearly seen, the chemical structure of Plast-A is similar to the chemical structure of DEHP, as an indication of the compatibility and potential of these palm oil-based compounds to serve as plasticizer for PVC. As both compounds contain bulky aromatic ring, it will increase more space between the PVC chains.

Besides that, the presence of ester groups will improve the interaction between plasticizer and PVC. Meanwhile, the hydrocarbon chain will render the bond holding force between the PVC chains.

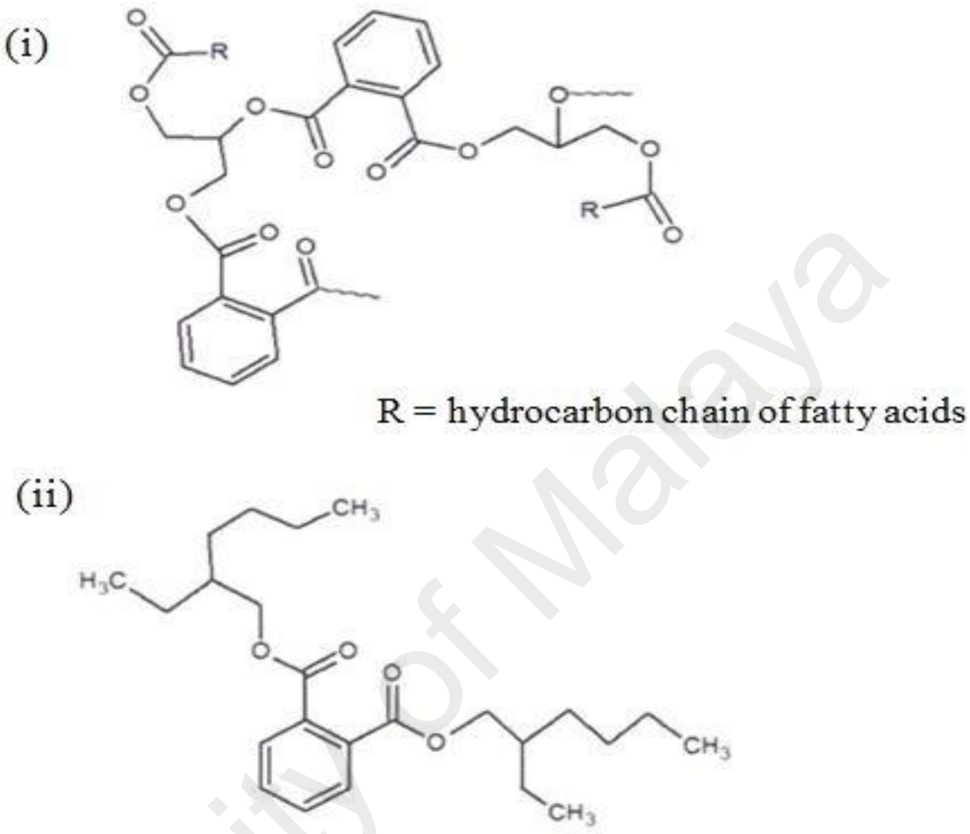


Figure 4.4: Chemical structure of (i) palm oil-based plasticizer (Plast-A) and (ii) DEHP plasticizer

4.1.5 Thermogravimetric analysis (TGA)

Figure 4.5 displays the comparison of derivative weight thermograms between Plast-A and Plast-D at heating rate 20°C/min. From the curves, it can be clearly seen that there was a slight difference in value of T_p between these polymeric plasticizers, with T_p of Plast-A showing higher value which indicates high rate of weight loss took place at temperature relatively higher than that of Plast-D. This suggests that the former has higher thermal stability than the latter. Thermal degradation of these plasticizers also can be determined by the loss of weight during heating. The total loss weight of

Plast-D was higher than Plast-A. The thermal degradation was affected by the chemical compositions and molecular weight of the alkyds.

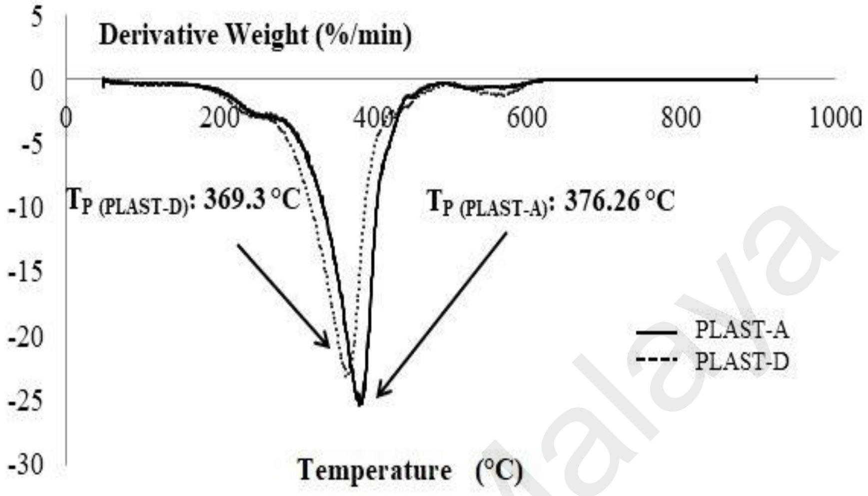


Figure 4.5: TGA spectrum of Plast-A and Plast-D

4.1.6 Toxicity test

Figure 4.6 illustrates the value of brine shrimp eggs hatched after they were immersed in salt solution (NaCl solution) which contaminated with different types of plasticizer, either DEHP or Plast-A. Figure 4.7 shows the images of shrimp larvae and eggs which captured by digital microscope. The brine shrimp eggs were left in the incubator for 3 days and then the mean of eggs hatched was recorded. According to the result, the number of brine shrimp eggs hatched in working solution contaminated with palm oil-based plasticizer is higher compared to that contaminated with DEHP plasticizer. Therefore, based on the higher number of eggs hatched, the palm oil-based plasticizer can be regarded as environmentally friendly and less toxic compared to DEHP.

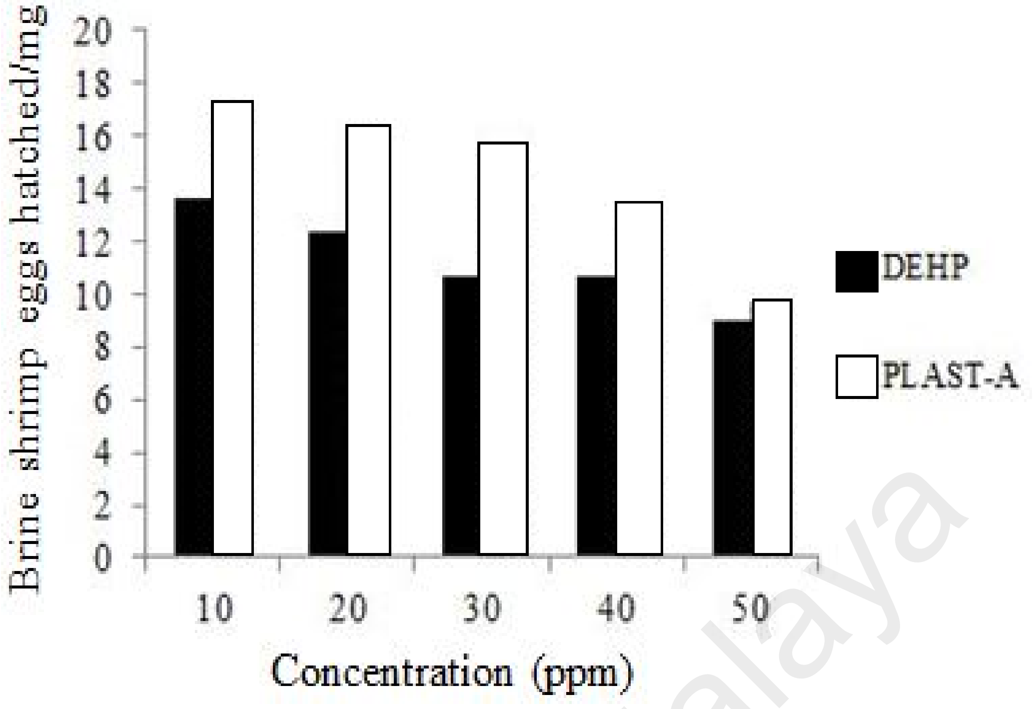


Figure 4.6: Brine shrimp eggs hatched in plasticizers

Figure 4.7: Eggs and larvae of brine shrimp eggs under digital microscope

4.2 Plasticized poly(vinyl chloride)

4.2.1 Thermogravimetric analysis (TGA)

Thermogravimetric analyzer (Model: TGA 6, Perkin Elmer) was used to identify the thermal stability of pure PVC and plasticized PVC (5% w/w loading). Each analysis was conducted from 50°C to 900 °C at different heating rates; 10, 15, 20, 25, 30 °C/min in N_2 atmosphere. The activation energy was determined and compared by using 2 methods, Kissinger and Flynn-Wall-Ozawa equations.

a) Kissinger Method

Figure 4.8 shows the derivative TGA thermograms of PVC-D5. The maximum rate of decomposition (T_p) for each scan range from 10 to 30 °C/min was recorded. The activation energy, E_d for each sample was obtained by plotting -ln (q/T_p^2) against 1000/T_p. The E_d was calculated from the value of gradient from the plot. The same trend of derivative TGA thermograms has been shown for other palm-oil based plasticized PVC where T_p increases with scan rate.

Table 4.2 reveals the E_d each of the pure PVC and plasticized PVC films. It can be clearly seen that, once plasticizer was incorporated with pure PVC, the value of E_d became higher. This is due to the chain entanglement of C=C in the plasticizers. Thus, the double bond presence in these plasticizers might contribute a good thermal stability. The highest molecular weight polymeric plasticized PVC which is PVC-A5 has highest thermal stability than other plasticized PVC. Similar results were reported when epoxidized soybean oil which is also polymeric plasticizers has been found to have good thermal stability by having its epoxy group to consume the HCl produced during dehydrochlorination at high temperature (Karmalm et al. 2009). In this palm oil-based plasticizer, the presence of C=C in fatty acids of palm oil has scavenge some of the radicals produced during degradation therefore, improve its thermal stability (Boguslaw et al. 2011). However, thermal stability for common plasticized PVC, PVC-ATEC5 and PVC-DHEP5 showed lower value than polymeric plasticizers.

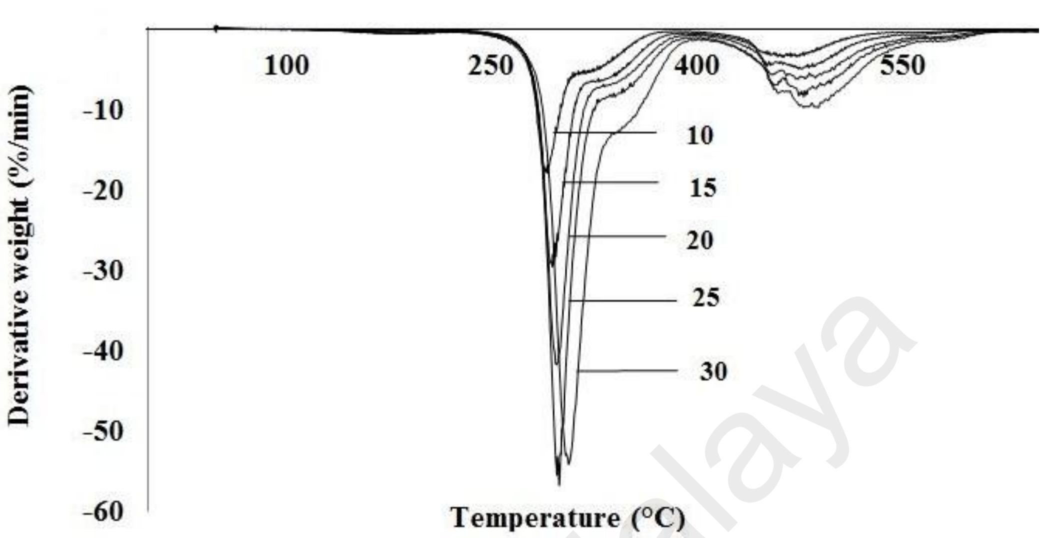


Figure 4.8: Derivative TGA thermogram of PVC-D5 at different heating rates

Table 4.2: Activation energy decomposition of plasticized PVC based on Kissinger method

q(K/min)	T_p (K)						
	PVC-A5	PVC-B5	PVC-C5	PVC-D5	PVC-ATEC5	PVC-DEHP5	PVC
10	558	554	558	563	559	558	567
15	560	558	563	568	561	569	565
20	562	564	568	573	564	573	581
25	568	569	576	578	573	581	582
30	573	572	577	588	580	581	584
Activation energy **E_d (kJ/ mol)**	**163.6**	**141.5**	**129.7**	**113.1**	**111.9**	**112.7**	**109.2**

b) Flynn-Wall-Ozawa Method

The activation energy, E_d was determined using data of weight loss against temperature. Unlike Kissinger method, the activation energy can be identified by including reaction order, meanwhile for Flynn-Wall-Ozawa method the activation energy can be obtained by conversion values from the graph of weight percent versus temperature as shown in Figure 4.9 (Ruowen et al. 2005). E_d for all the samples with different conversions were calculated from gradient by plotting log β versus 1000/T, where β is the heating rate, T is the temperature at different heating rates under the same conversional rate. Table 4.3 shows the value of E_d obtained using this Flynn-Wall-Ozawa equation which is comparable with Kissinger approach. PVC-A5 shows the highest activation energy followed by PVC-B5, PVC-C5 and PVC-D5 suggesting both methods, Kissinger and Flynn-Wall-Ozawa agree that the higher molecular weight plasticized PVC has high thermal stability than lower molecular weight plasticized PVC.

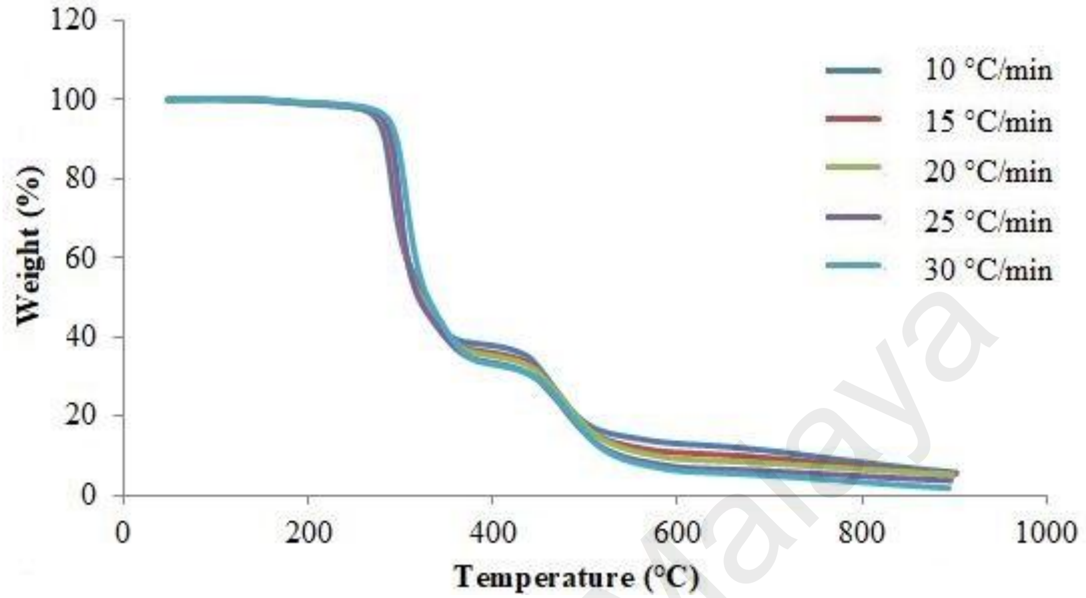


Figure 4.9: TGA curves of PVC-D5 at different heating rates

Table 4.3: Activation energy decomposition of plasticized PVC based on Flynn-Wall-Ozawa method

Conversion	**Activation energy (kJ/mol) of** PVC films						
	PVC-A5	PVC-B5	PVC-C5	PVC-D5	PVC-ATEC5	PVC-DEHP5	PVC
0.30	183.3	149.9	105.2	83.0	101.5	56.5	47.2
0.50	95.7	112.7	116.7	158.3	136.4	185.9	108.5
0.70	163.5	129.7	105.7	130.8	16.3	110.8	119.4
0.90	92.2	96.93	125.4	28.7	136.9	40.9	115.4
Mean	**133.7**	**122.3**	**113.3**	**100.2**	**97.8**	**98.6**	**97.6**

4.2.2 Differential scanning calorimetry (DSC)

Figure 4.10 shows the DSC thermogram of the unplasticized and plasticized PVC. The glass transition temperature, T_g of pure PVC is reduced by the addition of plasticizer. The T_g of plasticized PVC were recorded; 68.2 °C for PVC-A20, 66.3 °C for PVC-B20, 65.2 °C for PVC-C20 and 64.1 °C for PVC-D20. Meanwhile, the T_g for plasticized PVC with monomeric plasticizer which PVC-DEHP20 and PVC-ATEC20 are 58 ^{o}C and 55 ^{o}C, respectively. It indicates that the decreasing in T_g of the plastic is slightly lesser compared to PVC-DEHP20 and PVC-ATEC20. The smaller size of monomeric plasticizer is able to penetrate better to accommodate the space between the PVC chains compared to polymeric plasticizer. Furthermore, the T_g result from four palm oil-based plasticizers indicates that smaller size plasticizer tend to have better plasticizing ability and efficiency. PVC plasticized with Plast-D which is the smallest in weight has the lowest T_g, while those plasticized with higher M_w ones have relatively higher T_g.

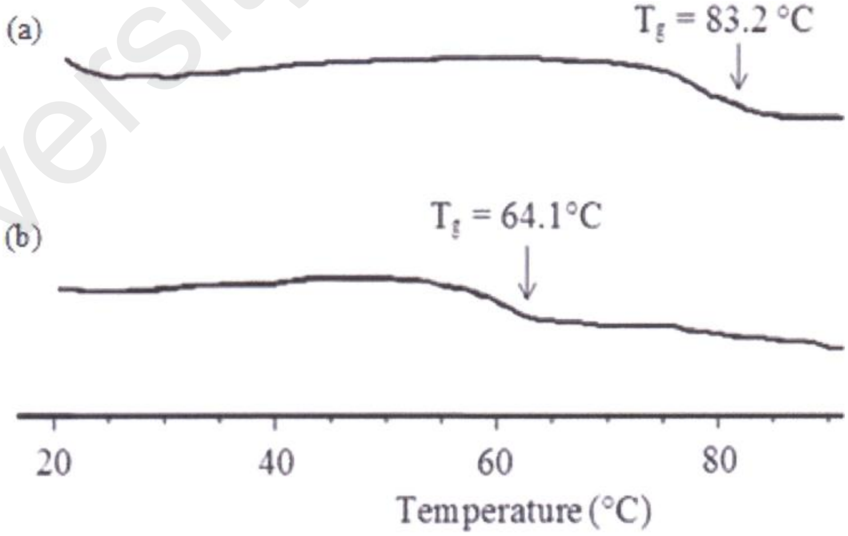


Figure 4.10: DSC thermogram of (a) Unplasticized PVC and (b) PVC-D20

4.2.3 Migration resistance test

UV-Vis spectrometer analysis has been done to study the leaching resistance of plasticizers in PVC films. n-Hexane and ethanol/water were 2 solvents used in this study which have different polarity. The ethanol/water has high polarity than n-hexane solvent. The plasticized PVC samples (1cm x 1cm) were placed in 5mL of n-hexane in a closed sample vial. Then, the samples were heated at 50 °C in oven to increase the migration rate of the plasticizers in the films. After 7 days, the n-hexane for each samples were analyzed by a UV-Vis spectrometer. Weight of PVC specimens was recorded before and after the test to identify the weight loss corresponding to leaching of plasticizers from the film.

Migration and leaching resistance test was further studied using ethanol/ water as a solvent. The ratio used for ethanol and water was 2:8 by volume. By the same method with n-hexane, the small and closed sample vials contained of 10 ml ethanol/water solvent were used to place PVC samples (1cm x 1cm). In order to maximize the rate of migrations of the plasticizers in the PVC, the oven was set up to 70 °C and all the samples were put in it for 1 week. Then, ethanol/water solvent for each samples were analyzed by UV-Vis spectrometer.

UV-Vis spectra in Figure 4.11 and 4.12 show the peak at 199 nm which attribute to the presence of ester group. From Figure 4.11, PVC-D20 sample recorded the highest 199 nm peak, indicates that the highest amount of plasticizers has leached out into the solvent during the immersion. The intensity of the peak decreases with increase in the molecular weight of the plasticizers used, with PVC-A20 sample having the lowest peak intensity. Figure 4.12 shows that PVC-DEHP15 has highest peak at 199nm than other plasticized PVC. It is possible that PVC-DEHP15 has highest intensity of peak because it is a monomeric plasticizers compared to PVC-D15 which is a polymeric plasticizers.

The polymeric plasticizers tend to retain longer in the PVC matric compared to those with monomeric plasticizers.

Figure 4.13 and 4.14 reveal the UV-Vis spectra of ethanol/water after migration resistance test for pure PVC and plasticized PVC at 20% w/w and 15% w/w loading respectively. The pure PVC shows no peak, thus the intensity of the peaks shows the extent of migration of plasticizers from PVC films that has taken place. Figure 13 reveals the peaks at 201 nm, 209 nm, 208 nm and 213 nm for PVC-A20, PVC-B20, PVC-C20 and PVC-D20 respectively which indicate the presence of ester group. As shown in the Figure 4.13, PVC-D20 sample which has the lowest molecular weight recorded the highest intensity of peak than other plasticized PVC films. In a nutshell, the decreasing in the molecular weight of plasticizers used has led to the increment of intensity of the peak.

Figure 4.14 shows the peaks at 201 nm, 207 nm, 202 nm, 203 nm and 208 nm for PVC-A15, PVC-B15, PVC-C15, PVC-D15 and PVC-DEHP15, respectively which also reflects the existence of ester group. Same result from Figure 4.12, it can be clearly seen from Figure 4.14 that PVC-DEHP15 has highest intensity of peak than PVC-D15. After 1 week immersed in n-hexane and ethanol/water, the plasticized PVC films (both 15% and 20%) were removed and dried in vacuum oven for 7 days and the weight of dried films were recorded. Table 4.4 and 4.5 show the weight change of films after immersion in n-hexane and ethanol/water, respectively. Weight of PVC samples decreased due to the migrating of plasticizers from PVC into the solvents. Among palm oil-based plasticizers, PVC-D indicated the highest weight loss, while PVC-A recorded the lowest weight loss. However, when comparing between the palm oil-based plasticized PVC and common plasticized PVC, the PVC-DEHP has higher weight loss.

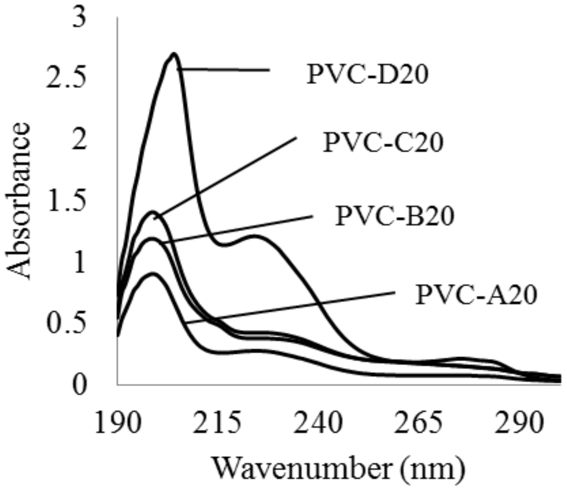


Figure 4.11: Spectrum of UV-Vis of n-hexane solvent after migration resistance test of 20% w/w loading

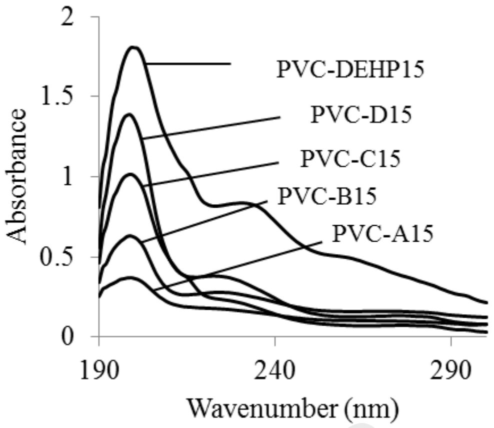


Figure 4.12: Spectrum of UV-Vis of n-hexane solvent after migration resistance test of 15% w/w loading

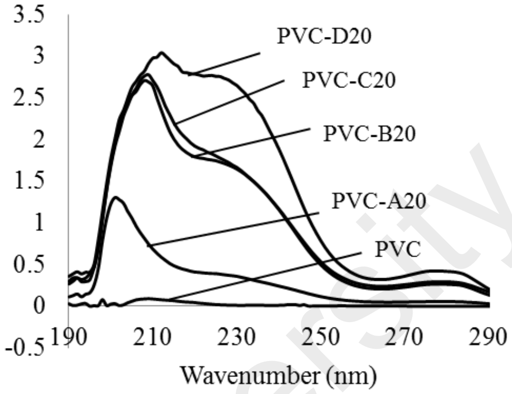


Figure 4.13: Spectrum of UV-Vis of ethanol/water solvent after migration resistance test of 20% w/w loading

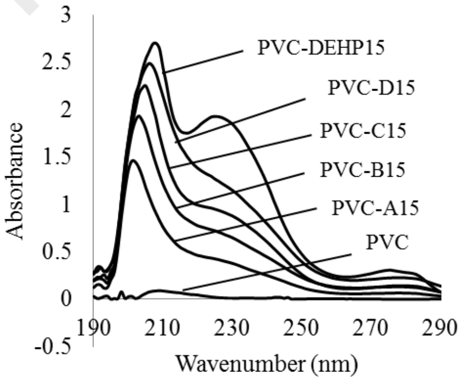


Figure 4.14: Spectrum of UV-Vis of ethanol/water solvent after migration resistance test of 15% w/w loading

Table 4.4: Weight of plasticized PVC film before and after immersed in n-Hexane for 1 week

Plasticized PVC	**Weight of PVC film before immersion / mg**	**Dried weight of PVC film after immersion / mg**	**Weight loss / %**
PVC-A20	21.50	20.90	2.8
PVC-B20	21.30	20.53	3.6
PVC-C20	21.80	20.22	7.3
PVC-D20	21.20	19.05	10.1
PVC-A15	21.10	20.62	2.3
PVC-B15	21.40	20.72	3.2
PVC-C15	21.60	20.11	6.9
PVC-D15	21.70	19.64	9.5
PVC-DEHP15	21.00	18.42	12.3

Table 4.5: Weight of plasticized PVC films before and after immersed in ethanol/ water for 1 week

Plasticized PVC	Weight of PVC film before immersion / mg	Dried weight of PVC film after immersion / mg	Weight loss / %
PVC-A20	14.01	13.55	3.3
PVC-B20	14.42	13.43	6.9
PVC-C20	14.51	13.25	8.7
PVC-D20	13.90	12.01	13.6
PVC-A15	14.60	14.24	2.5
PVC-B15	14.23	13.47	5.3
PVC-C15	13.61	12.58	7.7
PVC-D15	14.32	12.47	12.9
PVC-DEHP15	14.54	12.46	14.3

4.2.4 Tensile strength test

The study on the effects of molecular weight of polymers on mechanical properties has been done by many researchers (Stark et al. 2005; Bao et al. 2000). In this work, the mechanical properties such as tensile strength, elongation at break and elastic modulus are significantly influenced by molecular weight of plasticizer in PVC matrix. Table 4.1 (page: 30) and Figure 4.15, 4.16, 4.17 revealed the relationships between molecular weight of plasticizer in PVC matrix and the effect on mechanical properties.

Tensile strength, percentage elongation at break and elastic modulus of plasticized PVC at 10%, 15% and 20% loading are presented in Figure 4.15, 4.16 and 4.17, respectively. Based on the graphs, it can be clearly seen when palm oil-based plasticizer was introduced in the PVC matrix, the mechanical properties of plasticized PVC became enhanced. One of the possible reasons because due to the chain entanglement between the plasticizer and PVC matrix.

Figure 4.15 (a), Figure 4.16 (a) and Figure 4.17 (a) demonstrate the result for tensile strength. The tensile strength for PVC-A10, PVC-B10, PVC-C10 and PVC-D10 were 27.46 MPa, 24.46 MPa, 23.48 MPa and 18.64 MPa, respectively. The result shows that tensile strength decreased when the molecular weight of the plasticizer decreased. Plasticized PVC at 20% loading exhibits the same trend. The higher molecular weight plasticized PVC has indicated higher tensile strength. Presumably, Plast-A has more entanglement and intermolecular attraction with PVC matrix than Plast-B, C and D (Lim et al. 2015).

In general, percentage elongation at break will decrease when tensile strength increase (Azman et al. 2005). However, in this study percentage elongation at break in Figure 4.15 (b), 4.16 (b) and 4.17 (b) have the same trend with tensile strength.

Percentage elongation at break for unplasticized PVC was 18.51 % and improved by 48.51 % for PVC-A10 but became deteriorated to 40.10 %, 35.30% and 32.24 % for PVC-B10, PVC-C10 and PVC-D10 respectively as the molecular weight of plasticizer decreased. Percentage elongation at break at 20% loading displayed a slight decrease when compare with pure PVC. One of the possible reasons is the set of specimens were not homogeneously mixed that can cause plasticizer agglomerate and did not bind with PVC chain properly.

Figure 4.15 (c), 4.16 (c) and 4.17 (c) presented the elastic modulus for 10%, 15% and 20% loading. It shows that as the molecular weight of plasticizer increased, the elastic modulus also increased suggesting that the incorporation of plasticizer in PVC matrix with different molecular weight can improve the mechanical properties. Palm oil-based plasticizer and PVC matrix tend to hold each other more tightly when molecular weights of polymeric plasticizer increase. Therefore chain entanglement between plasticizer and PVC matrix will develop which can lead to enhancement of mechanical properties.

Meanwhile, the tensile strength, elongation at break and elastic modulus for DEHP-plasticized PVC were lower than palm oil-based plasticized PVC. It is because of plasticizer DEHP has small molecules because it is monomeric plasticizer compare to palm oil-based plasticizer which is polymeric plasticizer. The arrangement molecules of polymeric plasticizer can cause entanglement with PVC chains better than monomeric plasticizer.

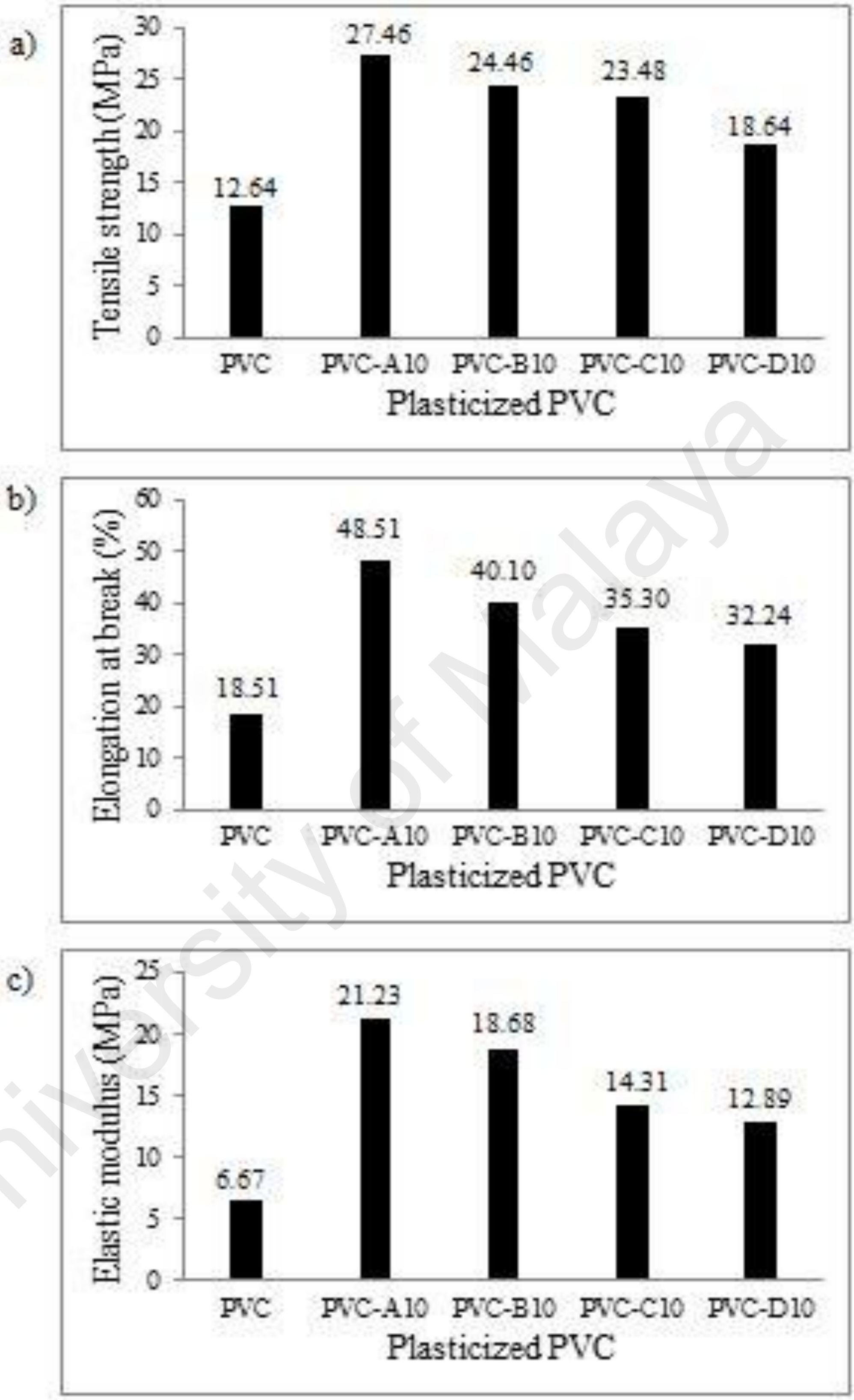


Figure 4.15: (a) Tensile strength (b) Elongation at break (c) Elastic modulus of unplasticized and plasticized PVC (loading 10%)

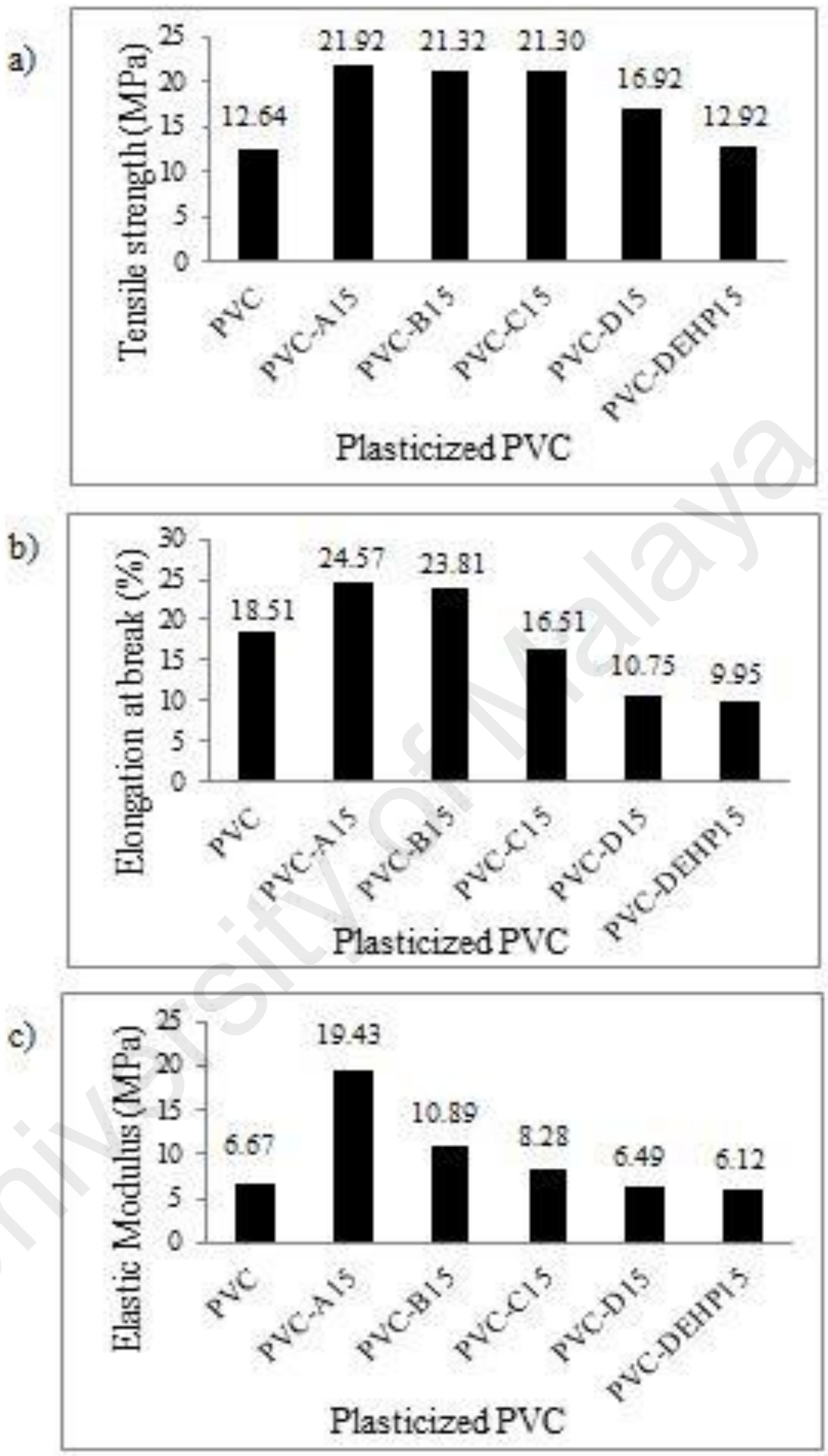


Figure 4.16: a) Tensile strength b) Elongation at break c) Elastic modulus of unplasticized and plasticized PVC (loading 15%)

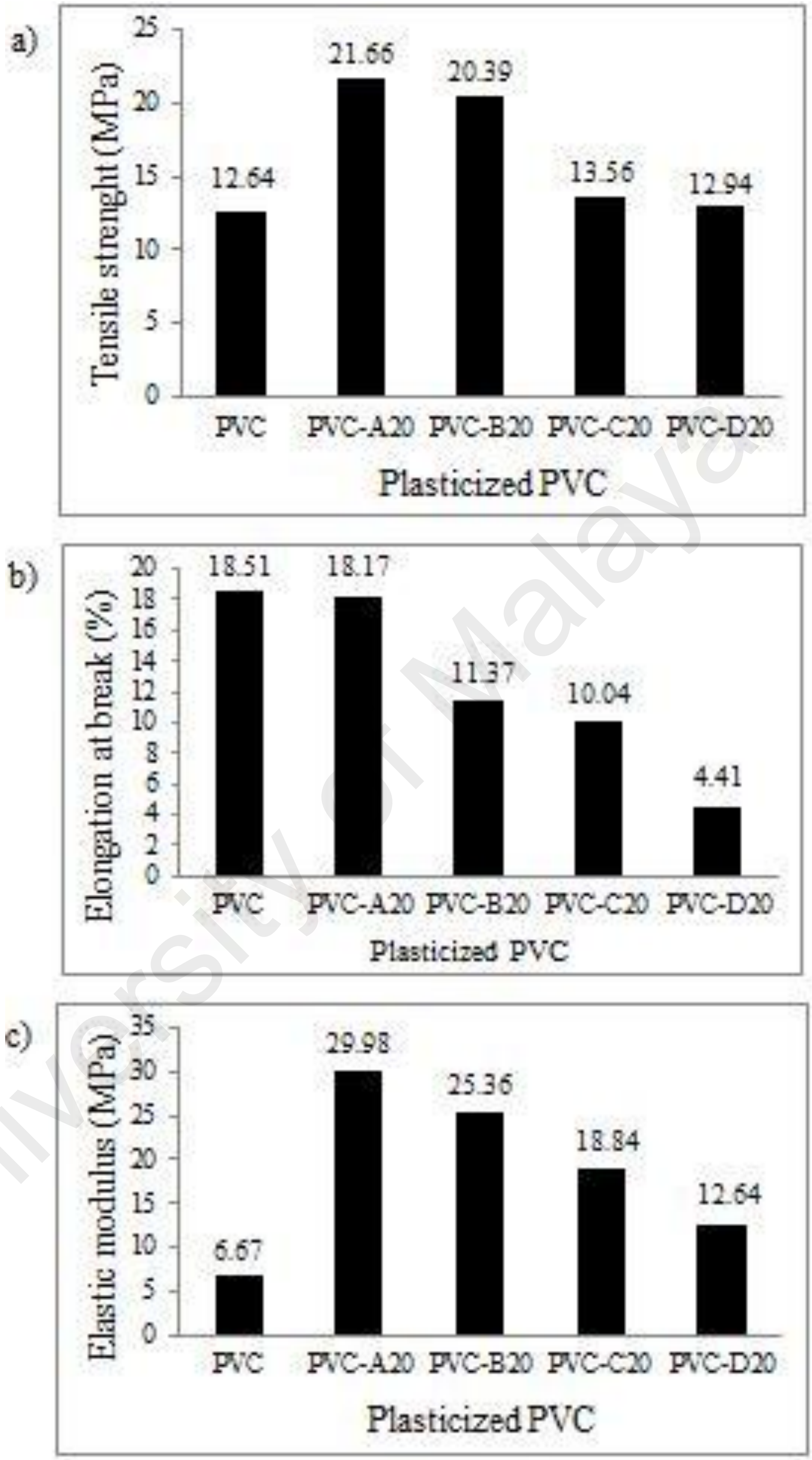


Figure 4.17: a) Tensile strength b) Elongation at break c) Elastic modulus of unplasticized and plasticized PVC (loading 20%)

4.2.5 FESEM analysis

The surface images of PVC with different molecular of plasticizers weight under 11,000X magnifications are shown in Figure 4.18. It can be clearly seen that when PVC was plasticized with lower molecular weight plasticizer, the presence of white spots and crumples becomes decrease. The white spots and crumples in the images are attributed to the crystalline regions in the plastic (Azman et al. 2005). Besides that, amorphous (non-crystalline region) makes the polymer film more flexible, meanwhile the crystalline region in PVC is refer to the rigidity and brittleness of the polymer (Zheng et al. 2007; Sin et al. 2014). The FESEM analysis indicates that lower molecular weight plasticizer is better in penetrating into the PVC chain networks compared to the higher molecular weight.

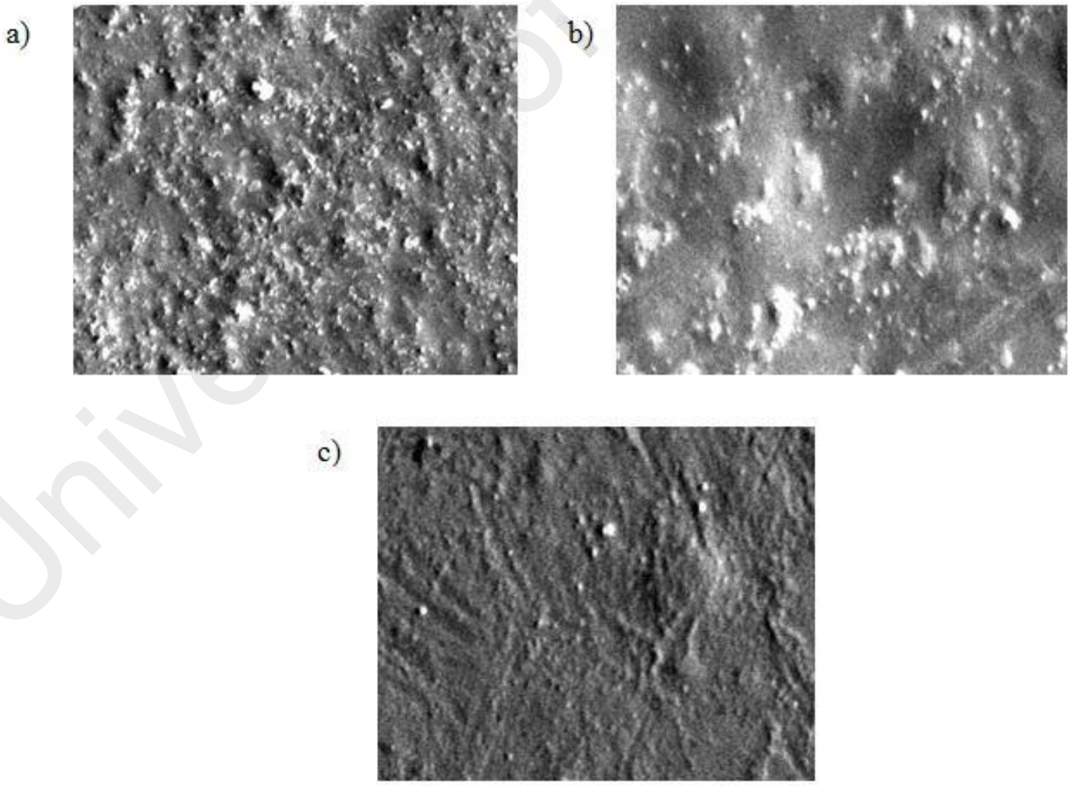


Figure 4.18: FESEM micrographs of a) PVC-A15, b) PVC-D15 and c) PVC-DEHP15

CHAPTER 5

CONCLUSION AND FURTHER WORK

5.1 Conclusion

Different molecular weights of environmentally friendly oil-modified polyester for PVC have successfully synthesized in this study. The effects of different molecular weight polymeric plasticizers on mechanical properties, thermal stability of PVC, plasticizing ability, and migration properties were investigated. FTIR and NMR results indicated the similarity of common plasticizer, DEHP and palm oil-based plasticizer which promoted the latter to be one of the alternatives plasticizer for PVC. The thermal stability resulted from TGA analysis showed the higher molecular weight plasticized PVC has higher activation energy of decomposition (E_d) and vice versa. The glass transition (T_g) of PVC incorporated with palm oil-based plasticized has deteriorated compared to pure PVC. The DSC analysis showed the lowest molecular weight plasticized PVC tends to have the lowest T_g which reflects to a good plasticizing ability. From the leaching resistance test, the higher molecular weight plasticizer has lower migration from PVC matrix compared to lower molecular weight plasticizer. FESEM analysis showed the good incorporation of plasticizer in the PVC polymer. This concludes that the properties of PVC plasticized with palm oil-based plasticizer can be varied by employing the molecular weight of the plasticizers as variable.

5.2 Suggestions for further work

1. Study of compatible coating for medical tube’s inner layer

Medical tube used for blood transfusion often ended up as bio-hazardous waste due to incapable of disposing the dripped blood inside the tube. By studying compatible coating between PVC medical tube and blood which can be treated and replaced after the blood contact, the dangerous waste will be reduced. The compatible coating will act as medium and restrict the blood migrates to medical tube surface, which mean the medical tube will not get contact with blood during the presence of coating. Instead of treat it as bio-hazardous waste, a treatment can be done by replacing the blood-contacted coating to a new one. Hence, after the treatment, it will no longer act as dangerous waste, instead the medical tube can be used again with no worries.

2. Study the sustainability of marine life in presence of palm oil-based plasticizer.

Marine life is facing dangerous state where they often consumed human disposed waste that threatens their life. Until now, there is no official solution how to eliminate that threat. During this research was conducted, one of test involved was hatching the brine shrimp egg in the presence of palm oil-based plasticizer. This proves that even in pure palm oil-based plasticizer, the marine life is not harmed. A further research should be studied where the palm oil-based plasticizer present in common polymer matrix can behave the same way, which cause no harms to the cycle of marine life.

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