

# Environmentally Friendly Oil-Modified Polyesters as Polymeric Plasticizers for Poly(vinyl chloride)

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**Abstract** Oil-modified polyesters were synthesized to serve as polymeric plasticizers for PVC. A total of four polymeric plasticizers with different average molecular weights were prepared. Characterizations were done using Fourier-transformed infrared spectroscopy, proton nuclear magnetic resonance spectroscopy, and gel permeation chromatography. Some of the tests conducted on PVC films include thermal stability test using thermogravimetric analyser, determination of glass transition temperature ( $T_g$ ), plasticizer migration and leaching resistance test, morphology study of plasticized PVC films using 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 20 wt% loading. The polymeric plasticizer is also able to contribute positively to the thermal stability and mechanical properties of the PVC films. Some of the advantages of incorporating polymeric plasticizer with high molecular weight includes lower rate of leaching from plastic, and improved tensile strength and elongation at break. Besides, thermal stability of the plastic studied using Kissinger's and Flynn–Wall–Ozawa's approaches shows that PVC blended with high molecular weight oil-modified polyester is more thermally stable, evidenced by the increase in the activation energy of decomposition,  $E_d$ . Toxicity test using brine shrimp egg shows encouraging results, where the oil-based plasticizer is considerably less toxic compared to some of the commercial plasticizers.

**Keywords** Bio-based polymer · Polymeric plasticizer · PVC · Thermal stability · Molecular weight · Environmentally friendly

## Introduction

PVC is one of the most widely produced plastics and has many important applications in various industries. It is used to produce various food packaging, toys, and medical apparatus such as urine bags, tubing systems and gloves [1, 2]. Uncompounded PVC is very rigid and is usually used as structural material in construction, as appliances in automotive industry, and pipes in sewer system [3]. For applications that require flexible PVC, the plastic is usually compounded with plasticizers. Besides, plasticizing PVC can also improve its workability, allowing it to be easily moulded into various shapes [4].

Plasticizer is a substance that is usually added into a polymeric material to produce homogeneous compound that are seemingly more flexible, softer, and easier to process than the polymer alone [5]. When plasticizer is incorporated into PVC, it deters the PVC polymer chains from closing into each other. This would generate more space between the polymer chains and deteriorate the bond holding between them. Consequently, each of the polymer chain is able to rotate and move more freely and render the plastic more flexible. Good plasticizer should be stable, cost-effective, compatible with PVC, and has low or no tendency to migrate or leach out from the polymer matrix. One of the most prevalent plasticizers used in PVC is dioctylphthalate, DOP or also known as DEHP. It is commonly used in the production of PVC plastic toys and blood bag [6]. However the migration and leaching of DEHP out from PVC has been a cause for concern as these

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chemicals could potentially cause harm to user's health. There are indications of transfer of plasticizers into a patient's bloodstream during blood transfusion [7]. Furthermore, clinical studies have indicated that DEHP could cause development of liver cancer in laboratory rats [8]. It is therefore important to have a plasticizer with low toxicity and good migration resistance to prevent or minimise transfer of these chemicals to end users.

In this work, palm oil is used as the main raw material to produce a polymeric compound which serves as plasticizer for PVC. Polymeric plasticizer is expected to be able to retain itself better in the plastic matrix due to stronger interaction with the PVC chain. Chain entanglement between the plasticizer and PVC reduces the tendency of the plasticizers to migrate or leach out from the plastic. However, one of the issues with the use of polymeric plasticizer is its limited compatibility with PVC. Although chain entanglement could improve the migration resistance of the plasticizer, it may also limit the plasticizing capability of the plasticizer. It is therefore important to have a better understanding on the effect of molecular weight of plasticizers on properties such as migration of plasticizers, compatibility, plasticizing capability and mechanical properties.

Besides leaching and migration of plasticizer from plastic, another problem commonly associated with PVC is its vulnerability to thermal degradation especially during high temperature processing. It is believed that PVC undergoes autocatalytic dehydrochlorination through free radical reaction at high temperature [9]. Many works were done to study the mechanism of thermal degradation of PVC and ways to improve its thermal stability. One example is from the work of Karmalm and Hjertberg, where they managed to improve the thermal stability of PVC by using epoxidized soybean oil (ESBO) as secondary plasticizer. The epoxy groups in ESBO are able to scavenge HCl which is believed to be one of the species that are responsible to propagate thermal degradation of the polymer [10, 11]. Interestingly, the use of palm oil-based compound as the polymeric plasticizer in this work is able to show some improvement in the thermal stability of the plastic as well. Presumably, the C=C from the unsaturated fatty acids in the palm oil-based compound could have played a role in scavenging the radicals produced during PVC degradation [12].

## Experimental

### Materials

Refined, bleached and deodorised palm oil was obtained from Yee Lee Edible Oils Sendirian Berhad. The following

materials were purchased from Sigma Aldrich (Steinheim, Germany): PVC (Molecular weight: 233,000 g/mol), ATEC, deuterated chloroform, potassium hydroxide (KOH), potassium phthalate monobasic (KHP), sodium chloride (NaCl), sodium bicarbonate (NaHCO<sub>3</sub>) and polyethylene glycol p-(1,1,3,3-tetramethylbutyl)-phenyl ether (triton X-100). Methanol, acetic acid, and chloroform were obtained from RCI Labscan Limited, phthalic anhydride from R&M Chemicals, Ca(OH)<sub>2</sub> from HmbG Chemicals. Tetrahydrofuran (THF) and glycerol from Friendemann Schmidt Chemical, while DEHP from MP Biomedicals, Inc (USA). Brine shrimp eggs (known as *Artemia Salina*) were obtained from Ocean Nutrition Europe. All the chemicals were used as received.

### Synthesis of Palm Oil-Based Plasticizers

A total of four palm oil-based compounds (codename Plast-A to Plast-D) with different molecular weights were synthesised according to the formulations shown in Table 1. The reaction setup involves a three-necked reaction flask equipped with a condenser, mechanical stirrer, and thermometer placed in a heating mantle. Mixture of palm oil, glycerol, and Ca(OH)<sub>2</sub> was allowed to undergo alcoholysis at 220 °C for 2 h. Subsequently, the temperature was reduced to 150 °C and phthalic anhydride was added slowly into the reaction mixture. The temperature was then raised back to 220 °C to allow polyesterification between the predominant mixture of monoglyceride and diacids to progress. In order to ensure comparable extent of reaction, each synthesis was conducted until the difference in the final acid value of the mixture is ≤2 mg KOH/g. The acid number test was performed based on ASTM D1639. Note that for Plast-C and Plast-D, acetic acid was added during the synthesis to endcap some of the excess –OH groups. This is important to ensure that the hydroxyl value of the compounds is comparable with each other.

### <sup>1</sup>H-NMR and FTIR Analyses

<sup>1</sup>H-NMR analysis on the palm oil-based plasticizer was conducted using NMR machine model ECX400MZ-JEOL.

**Table 1** Formulations of palm oil-based plasticizers

Components	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) <sub>2</sub> (×10 <sup>-3</sup> )	3.46	3.29	3.29	3.29

Samples for the  $^1\text{H-NMR}$  analysis were prepared by dissolving the palm oil-based compounds in deuterated chloroform (99.8 %  $\text{CDCl}_3$ ). Traces of tetramethylsilane (TMS) are present in the deuterated solvent to lock the signal of the analysis at 0 ppm. As for FTIR analysis, the machine used was FT-IR Spectrometer (Perkin Elmer, Frontier). The polymeric plasticizers were spread into thin film on a KBr cell and scanned from 400 to 4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ .

### Molecular Weight Analysis

Gel permeation chromatography (GPC) analysis was carried out to determine the molecular weight of the palm oil-based compounds. The samples were dissolved in THF and filtered through a PTFE membrane (0.45  $\mu\text{m}$ ) before analysis. Each analysis runs for 55 min using THF as eluent. The instrument was calibrated with monodispersed polystyrene standards prior to analysis. Viscosity test was conducted to compare the relative viscosity of the polymeric plasticizers. The viscosity of the samples can be used to reflect the relative molecular weight of the plasticizers. The test was conducted using Ubbelohde viscometer in water bath at 30 °C. The plasticizers were first diluted in toluene to produce solution with fixed concentration of 40 wt%. The flow time of each sample was recorded to determine the relative viscosity of the polymeric plasticizers. Glycerol was used as the standard.

### Plasticization of PVC

Plasticization of PVC was conducted using solution blending technique. THF was used as mutual solvent to dissolve PVC and the polymeric plasticizers prior to blending. The blending was conducted in water bath at 65 °C for 6 h. The mixture was then transferred into a petri dish and left to air-dry in fumehood for 24 h. The residual solvent in the films was removed by placing the films in vacuum oven for 96 h at 70 °C. The composition of plasticized PVC films is summarised in Table 2.

### Thermal Analysis

The thermal stability of plasticized PVC was investigated using a thermogravimetric analyser (Model: TGA 6, Perkin Elmer). Each analysis was conducted from 50 °C to 900 °C in  $\text{N}_2$  atmosphere at flow rate of 20 ml/min. The activation energy of decomposition ( $E_d$ ) of the samples was determined using Kissinger approach [13, 14]. Heating rates ( $q$ ) were varied from 10 to 30 °C/min and the peak decomposition temperature ( $T_p$ ) of each analysis was used to plot a graph of  $\ln(q/T_p^2)$  against  $1000/T_p$  to obtain the  $E_d$  of the sample. The thermal stability of PVC films obtained

from the Kissinger approach was compared with another method, Flynn-Wall- Ozawa approach [15]. The glass transition temperature ( $T_g$ ) of PVC films were obtained using DSC (Model: Q20, TA Instrument). The samples were scanned from 10 °C to 120 °C at heating rate of 20 °C/min under  $\text{N}_2$  atmosphere.

### Leaching Resistance Test

Leaching resistance test of plasticizers in PVC films was studied by placing PVC samples (1 cm  $\times$  1 cm) weighed  $21.5 \pm 0.3$  mg in 5 mL of n-hexane in a closed sample vial. The samples were then heated at 50 °C in oven to speed up the rate of migrations and leaching of the plasticizers in the plastics. After 7 days, the n-hexane for each samples were analysed by using UV-Vis spectrometer. Weight of PVC specimens was recorded before and after the test to determine the weight loss attributed to leaching of plasticizers from the plastic film. Migration and leaching resistance test were also conducted in a more polar solvent, ethanol/water mixture [16]. The ratio used for ethanol and water was 2:8 by volume.

### Mechanical Properties of PVC

The mechanical properties of plasticized PVC were carried out according to ASTM D882 [17] by using a Zwick/Roell Z030 (Model No. BZ030/TH25) with 5 kN load cell. 5 specimens for each sample were prepared by cutting the PVC films into same dimension of 100 mm  $\times$  10 mm while the gauge length was set at 50 mm. Micrometre screw gauge was used to measure the thickness of specimens. Each specimen was tested by same cross head speed of 50 mm/min. The result of tensile strength, elongation at break and modulus of elasticity for each PVC film specimen were calculated and obtained from chart of plotted stress-strain curve.

### FESEM Analysis

Field emission scanning electron microscope (FESEM) analysis was carried out to study the morphology of plasticized PVC films. The surface images of different molecular weight plasticized PVC were captured using HITACHI UHR FESEM (SU8820 Series) at an electron acceleration voltage of 2 kV.

### Toxicity Test

The toxicity of palm oil-based plasticizers and commercially available plasticizers, DEHP were compared using brine shrimp egg [18]. Stock solution of plasticizer was prepared by dissolving 0.1 g of plasticizers in 100 ml of

**Table 2** Compositions 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-Dhp5	95	–	–	–	–	5	–
PVC-Dhp20	80	–	–	–	–	20	–
PVC-Atc5	95	–	–	–	–	–	5
PVC-Atc20	80	–	–	–	–	–	20

2 % NaCl solution which was then adjusted to pH 8.3 with NaHCO<sub>3</sub>. About 0.02 ml of triton-X 100 was added into the solution to improve the solubility of plasticizer. The stock solution was diluted with 2 % NaCl solution and adjusted back to pH 8.3 to obtain working solutions of 10, 20, 30, 40 and 50 ppm. 2 mg of brine shrimp eggs were placed in petri dish, followed by (1) 2 % NaCl stock solution (to serve as control), or (2) working solutions (as experimental dishes). The dishes were placed in incubator at 26 °C, and the number of eggs hatched was recorded after 3 days.

## Result and Discussion

### Characterisation of Palm Oil-Based Plasticizers

Some of the properties of the palm oil-based plasticizers are shown in Table 3. Plast-A recorded the highest molecular weight 9560 g/mol, followed by Plast-B, Plast-C, Plast-D and monomeric plasticizer DEHP with molecular weight of 4787, 4663, 2279 and 390 g/mol respectively. Result from viscosity test agrees with the molecular weight of the compounds obtained from GPC analysis. Plast-A which has the highest molecular weight, recorded the highest relative viscosity, while Plast-D the lowest. The difference in the molecular weight of the 4 compounds is achieved by varying the ratio of diacid : OH equivalence in the formulation. In order to maintain comparable –OH group in the compound, acetic acid (monofunctional) was added in Plast-C and Plast-D formulations. The final acid value of the 4 plasticizers is similar, an indication that comparable extent of reaction has taken place in the synthesis of the 4 compounds.

<sup>1</sup>H-NMR and FTIR spectra of Plast-A is shown in Fig. 1a, b respectively. Peak around 7.7 ppm in the <sup>1</sup>H-NMR spectrum is attributed to the aromatic proton from incorporated PA, peak at 5.3 ppm is from the resonance of vinyl protons of unsaturated fatty acids, and peaks at 2.0 and 2.3 ppm are from –C=C–CH<sub>2</sub>– and –OOC–CH<sub>2</sub>–, respectively. Peaks in the region 0.9–1.4 ppm are attributed to resonance of protons from the hydrocarbon chain of fatty acids. Interpretation of the FTIR spectrum in Fig. 1b is consistent with the <sup>1</sup>H-NMR analysis. Among the functional groups notable include the –OH group at 3492 cm<sup>-1</sup>, –C=O stretching of ester at 1730 cm<sup>-1</sup>, and –C–O– stretching at 1278 and 1130 cm<sup>-1</sup>. Spectra for other palm oil-based plasticizers are not shown as they are similar to each other.

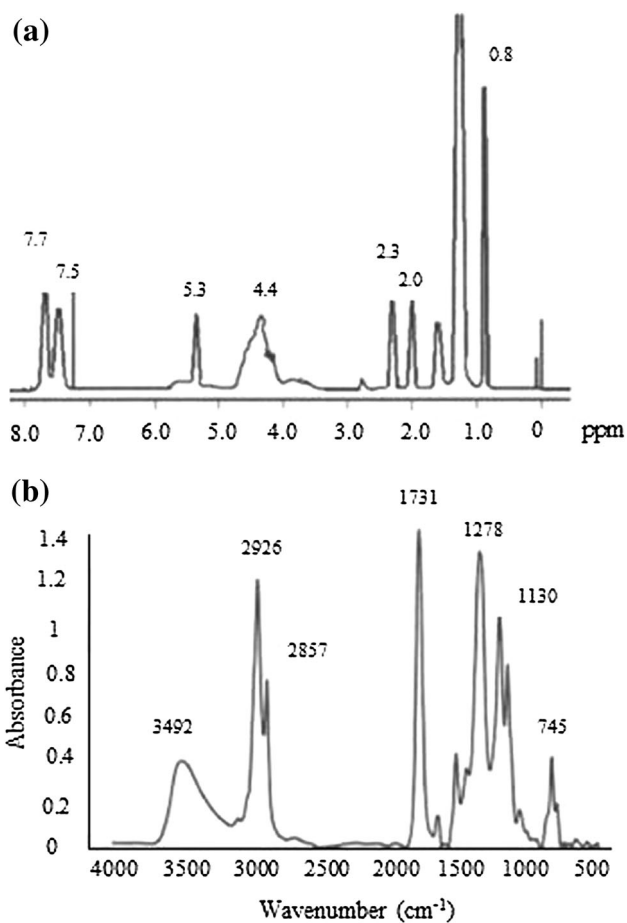
Figure 2 shows the plausible chemical structure of Plast-A interpreted from the spectroscopic analyses. The chemical structure of Plast-A is similar to the structure of DEHP, an indication of the compatibility and potential of these palm oil-based compounds to serve as plasticizer for PVC. Both compounds contain bulky aromatic ring which could help to generate more space between the PVC chains, ester groups to enhance interaction between plasticizer and PVC, and hydrocarbon chain to interrupt the bond holding force between the PVC chains.

### Thermal Analysis

Derivative TGA thermograms of PVC-D5 are shown in Fig. 3. Several scans with different heating rate (q), ranges from 10 to 30 °C/min were conducted and the temperature at maximum rate of decomposition (T<sub>p</sub>) for each scan was recorded. The activation energy, E<sub>d</sub> for each of the samples were obtained by plotting –ln (q/T<sub>p</sub><sup>2</sup>) against 1000/T<sub>p</sub>. The gradient from the plot is used to calculate the E<sub>d</sub>. The

**Table 3** Properties of palm oil-based plasticizers and DEHP

Properties	Plast-A	Plast-B	Plast-C	Plast-D	DEHP
Acid value/(mg KOH/g)	24.1	25.6	25.1	27.0	0.05
Molecular weight/(g mol <sup>-1</sup> )	9560	4787	4663	2279	390
Appearance	Dark brown Non-flowable	Dark brown Slightly flowable	Dark brown Viscous but flowable	Dark brown Viscous but flowable	Crystal Clear, flowable
Relative viscosity	10.2	7.48	5.44	4.35	–
Density/(kg/m <sup>3</sup> )	1516	1124	1122	1061	990

**Fig. 1** a <sup>1</sup>H-NMR spectrum of Plast-A, and b FTIR spectrum of Plast-A

derivatives TGA thermograms for other palm oil-based plasticized PVC exhibit the same trend where  $T_p$  increases with scan rate (not shown).

$E_d$  of plasticized PVC is shown in Table 4. Interestingly, a trend is observed where higher molecular weight plasticizers tend to contribute positively to the thermal stability of the plasticized PVC. Although the main function of plasticizer is to induce flexibility to plastic, the polymeric

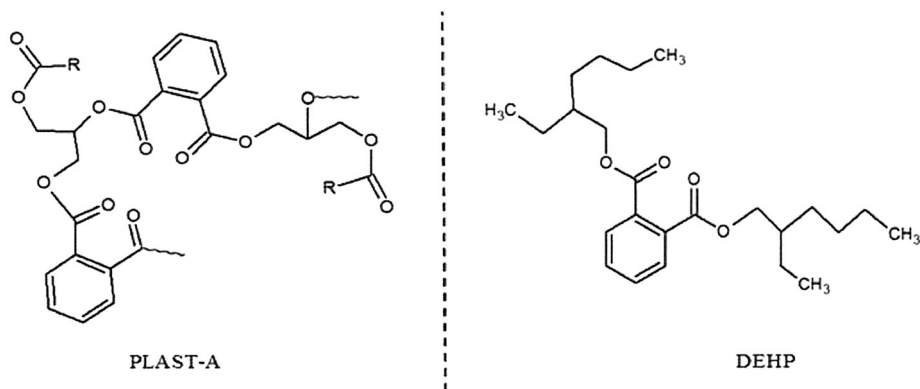
palm oil-based plasticizer was found to improve the thermal stability of the compounded plastic as well. Similar results are reported in the work of Karmalm and Hjertberg [10], where the use of epoxidized oil as plasticizer was found to improve the thermal stability of PVC by having its epoxy group to consume the HCl produced during dehydrochlorination at high temperature. In this palm oil-based plasticizer, it is likely that the C=C present in fatty acids of palm oil scavenge some of the radicals produced during degradation, thus improve its thermal stability [12].

Besides, the improvement in thermal stability of the plasticized PVC with molecular weight of the plasticizers suggests that the strength of the interaction between plasticizer and PVC may affect the thermal stability as well. Higher molecular weight plasticizers tend to entangle with PVC chains which could result with closer and stronger interaction between the two. It is noteworthy that earlier study [12] has indicated possible interaction between the –OH of palm oil-based plasticizer with C–Cl of PVC and this may slightly retard the dehydrochlorination process involving the C–Cl during thermal degradation. Table 5 shows the value of  $E_d$  obtained by using this Flynn–Wall–Ozawa equation which is comparable to the results obtained through Kissinger's approach. PVC-A5 shows the highest activation energy followed by PVC-B5, PVC-C5 and PVC-D5.

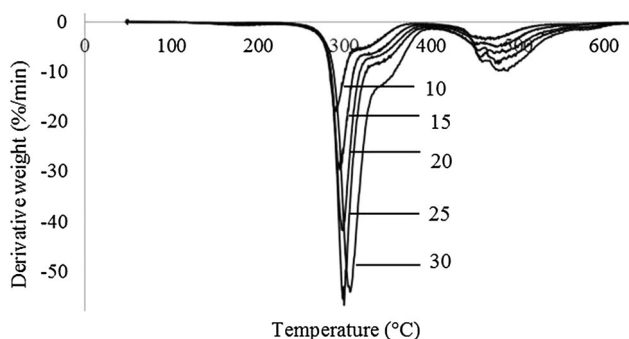
DSC thermogram of the plasticized PVC in Fig. 4 shows that addition of the polymeric plasticizers into PVC managed to reduce the  $T_g$  of the plastics. PVC plasticized with 20 wt% of palm oil-based plasticizers has decreased to 68.2 °C for PVC-A20, 66.3 °C for PVC-B20, 65.2 °C for PVC-C20 and 64.1 °C for PVC-D20. The reduction in the  $T_g$  of the plastic is slightly lesser compared to those plasticized with monomeric plasticizers, PVC-Dhp20 and PVC-Atc20 with  $T_g$  of 58 °C and 55 °C, respectively. This is not surprising as monomeric plasticizer which is smaller in size is known to be able to penetrate better to accommodate the space between the PVC chains. The trend observed in the  $T_g$  of the four palm oil-based plasticizers



**Fig. 2** Chemical structure of Plast-A and DEHP



\*R = hydrocarbon chain of fatty acids



**Fig. 3** Derivative TGA thermogram of PVC-D5 at different heating rates

agrees with the fact that smaller size plasticizer tend to have better plasticizing ability. PVC plasticized with Plast-D which is the smallest in weight has the lowest  $T_g$ , while

those plasticized with higher MW ones have relatively higher  $T_g$ . As indicated earlier, high MW plasticizer tend to entangle around the PVC chain and this could retard the mobility and freedom of the PVC chains, thus limit the plasticizing efficiency.

**Leach Resistance of Plasticizers in PVC**

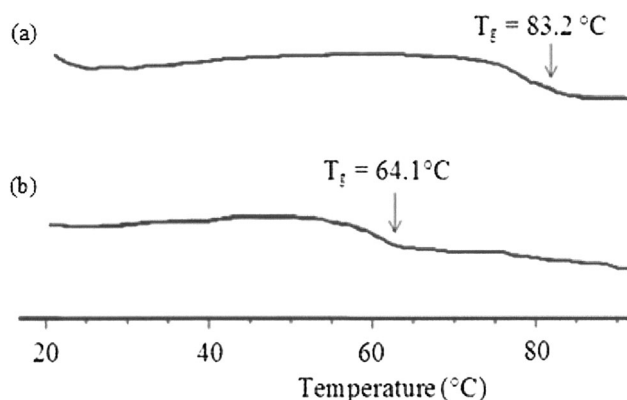
The extent of migration and leaching of plasticizers from PVC film was investigated by analysing the n-hexane and ethanol/water solvent which were used to immerse the plasticized PVC films with a UV–Vis spectrometer. UV–Vis spectra in Fig. 5a show presence of peak at 199 nm, attributed to the ester group of plasticizer. The figure shows that DEHP in PVC experienced the highest rate of leaching compared to the polymeric palm oil-based plasticizer. Chain entanglement and strong interaction between the

**Table 4** Activation energy of decomposition,  $E_d$  of plasticized PVC based on Kissinger’s equation

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

**Table 5** Activation energy decomposition,  $E_d$  of plasticized PVC based on Flynn–Wall–Ozawa method

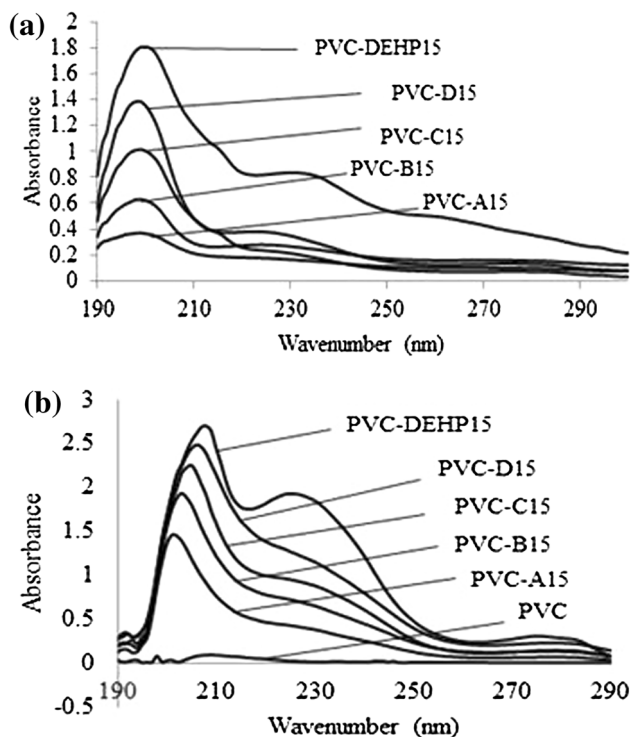
Conversion ( $\alpha$ )	Activation energy/(kJ/mol)						
	PVC-A5	PVC-B5	PVC-C5	PVC-D5	PVC-ATEC5	PVC-DEHP5	PVC
0.30	183.3	149.9	105.2	83.0	101.5	56.5	47.2
0.50	95.7	112.7	116.7	158.3	136.4	185.9	108.5
0.70	163.5	129.7	105.7	130.8	16.3	110.8	119.4
0.90	92.2	96.93	125.4	28.7	136.9	40.9	115.4
Mean	133.7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



**Fig. 4** DSC thermogram of *a* unplasticized PVC and *b* PVC-D20

plasticizer and PVC chain allows the plasticizer to retain longer in the PVC matrix. Amongst the PVC with polymeric plasticizer, PVC-D15 sample recorded the strongest peak at 199 nm, suggesting the highest amount of plasticizer has leached out into the solvent during the test. 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.

Similar trends were observed in the leaching test conducted in ethanol/water solution, shown in Fig. 5b. Monomeric plasticizer DEHP shows the strongest peak around 199 nm, followed by Plast-D, Plast-C and Plast-D.



**Fig. 5** UV-Vis spectra of *a* n-hexane solvent and *b* ethanol/water, after migration resistance test of PVC with 15 % w/w loading of plasticizers

Even in polar solvent, polymeric plasticizer shows better migration and leaching resistance. The solution from pristine PVC sample serves as control and it does not show any peak at 199 nm. This suggests that peak at 199 nm is indeed reflecting the ester group of plasticizer.

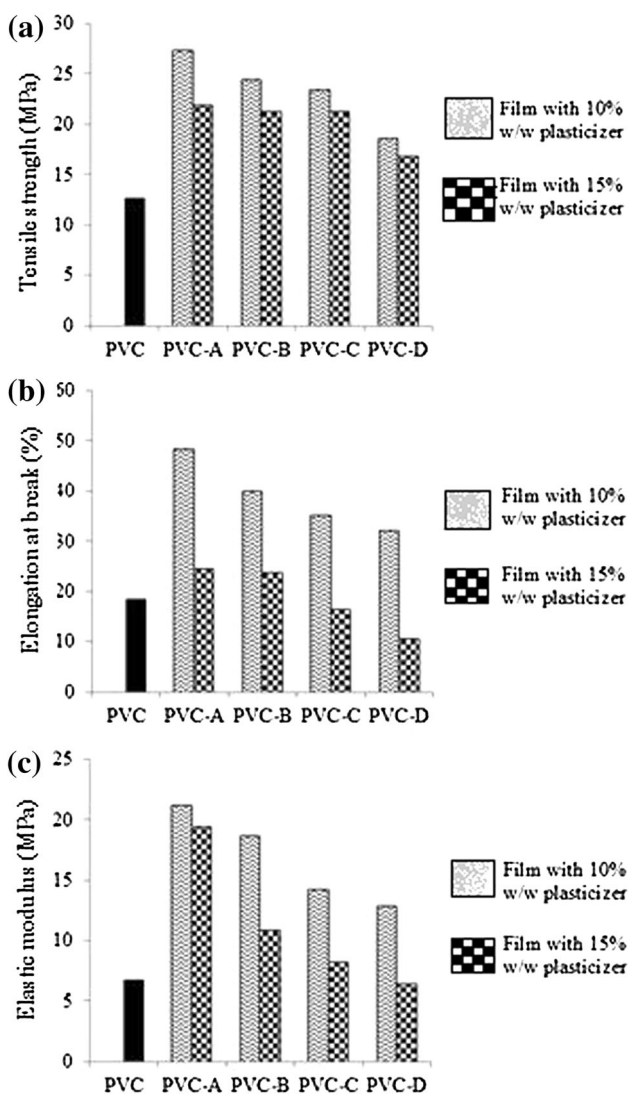
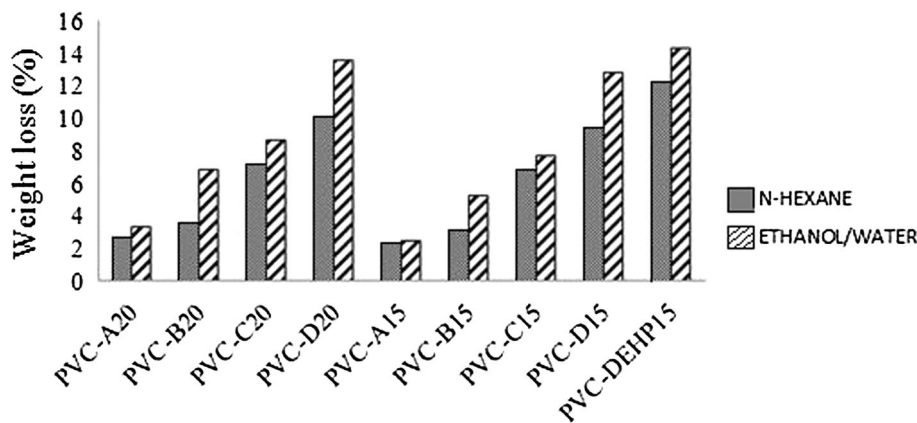
After 7 days immersed in n-hexane or ethanol/water solution, the PVC samples were removed and dried in vacuum oven for a week before measuring its constant weight. The weight change of the samples after the immersion is shown in Fig. 6. Weight of PVC samples decreased owing to the leaching of plasticizer from PVC into the solvent. Amongst all of the PVC films with palm oil-based plasticizers, PVC-D indicated the highest weight loss, while PVC-A recorded the lowest weight loss, and as expected, PVC-DEHP film shows the highest weight loss out of all the samples. The result is consistent with UV-Vis analysis, where higher molecular weight plasticizers tend to retain itself better in the plastic matrix compared to those with lower molecular weight.

### Mechanical Properties of PVC Films

Mechanical properties such as tensile strength, elongation at break, and elastic modulus of plasticized PVC are influenced by the molecular weight of the plasticizer used. Mechanical properties of PVC films blended with plasticizers of different molecular weights are shown in Fig. 7. Based on the chart, there is an obvious trend observed, where the mechanical properties of the plasticized films have improved after they were blended with higher molecular weight plasticizer. Figure 7a demonstrates the result for tensile strength of the plasticized PVC. The tensile strength of PVC-A10, PVC-B10, PVC-C10 and PVC-D10 are 27.46, 24.46, 23.48 and 18.64 MPa, respectively. Tensile measurement was carried out on PVC-DEHP15 as well, and the plastic recorded tensile strength of 12.92 MPa, significantly lower compared to those with polymeric plasticizers. The improvement in the tensile strength of the plastic is attributed to the strong interaction between the polymeric plasticiser with the PVC chains. The polar group of the plasticizer, such as the C=O and -OH group are able to interact with the C-Cl of PVC [14]. Besides, chain entanglement between the polymeric plasticiser and PVC chains could have contributed to the enhanced mechanical properties of the plastic as well [19].

Generally, percentage of elongation at break of a material will decrease when its tensile strength increase [20]. However, in this study, percentage elongation at break of the PVC plasticized with polymeric palm oil-based compound shows improvement as well. The results are shown in Fig. 7b. Percentage elongation at break for unplasticized PVC was at 18.51 %, and its value improved by an average of 20–30 % upon blending with the

**Fig. 6** Percentage weight loss of plasticized PVC film after immersion in n-hexane or ethanol/water

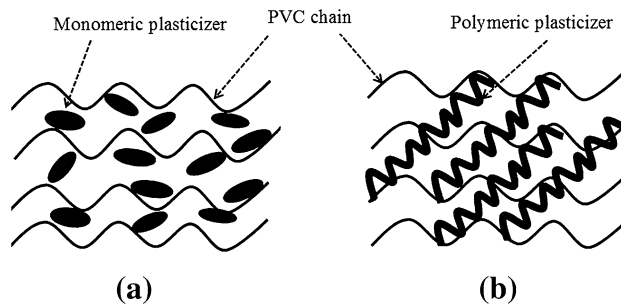


**Fig. 7** a Tensile strength, b elongation at break, and c elastic modulus of plasticized PVC films

polymeric plasticizers. PVC-A10 recorded the highest elongation at break, 48.51 %, while the elongation at break for PVC blended with DEHP is only at 9.95 %. The improvement could be attributed to the ability of the polymeric plasticizer to bind the PVC chains together, and resist them from separating. The proposed plasticizing mechanism of monomeric and polymeric plasticizer is shown in Fig. 8.

**Morphology Studies of PVC Films**

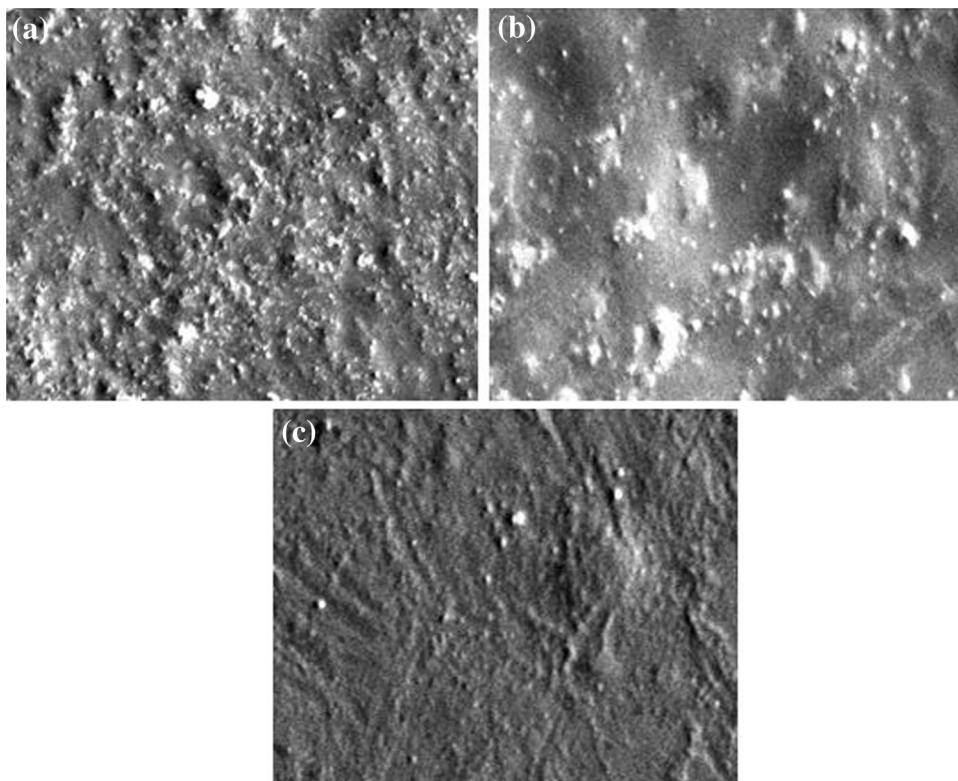
Figure 9 shows the surface images of plasticized PVC with different molecular weight at 11,000× magnifications. It can be seen that the presence of white spots and rumples decrease when PVC was plasticized with lower molecular weight plasticizer. The white spots and rumples in the images reflect the crystalline regions in the plastic [19]. As reported in many literatures, crystalline region in PVC is responsible for the rigidity and brittleness of the polymer, while the amorphous or non-crystalline region contributes flexibility to the polymer film [21, 22]. Result from FESEM analysis shows that lower molecular weight plasticizer is better in penetrating into the PVC chain networks



**Fig. 8** Proposed plasticizing mechanism of a monomeric plasticizer, and b polymeric plasticizer



**Fig. 9** FESEM micrographs showing surface morphology of **a** PVC-A15, **b** PVC-D15, **c** PVC-DEHP15



and disrupts the crystalline structure of the polymer. The result is also in agreement with DSC analysis where PVC-D tend to have lower  $T_g$  compared to PVC-A, and indication that the former has better film flexibility.

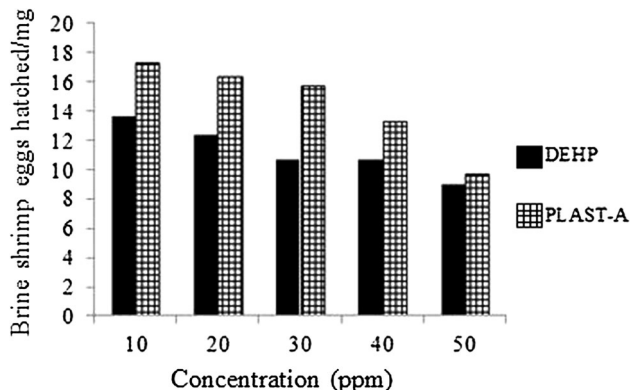
### Toxicity Test of Plasticizers

Figure 10 shows the number brine shrimp eggs hatched after they were immersed in NaCl solution contaminated with different types of plasticizer, DEHP or Plast-A. Digital microscope was used to capture the images of shrimp larvae and eggs, shown in Fig. 11. The mean number of

brine shrimp eggs hatched was recorded after they were left in the incubator for 3 days. The result shows that the number of brine shrimp eggs hatched in working solution contaminated with DEHP is lower compared to that contaminated with palm oil-based plasticizer. Based on the higher number of eggs hatched, the palm oil-based plasticizer can be regarded as less toxic compared to DEHP, and this also reflects the environmentally friendly aspect of this compound.

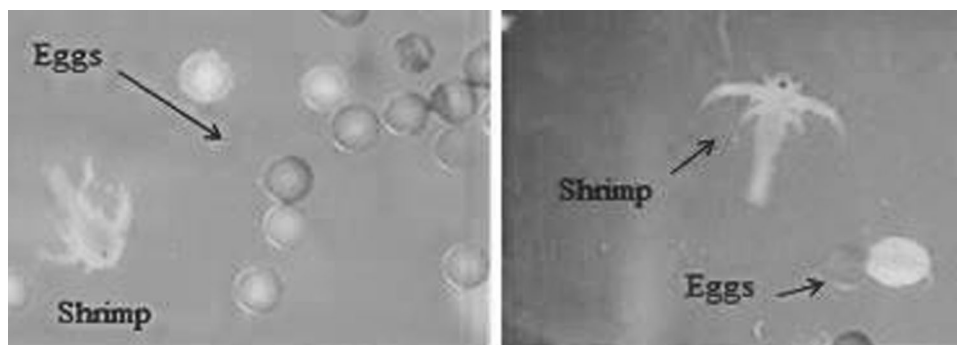
### Conclusion

Palm oil-based plasticizer for PVC with different molecular weights were synthesised by manipulating the ratio of diacid:  $-OH$  equivalent in the formulation. Plast-A recorded the highest molecular weight ( $9560 \text{ g mol}^{-1}$ ), followed by Plast-B, Plast-C and Plast-D with molecular weight of  $4787$ ,  $4663$  and  $2279 \text{ g mol}^{-1}$ , respectively. The effect of polymeric plasticizers with different molecular weight on thermal stability of PVC, plasticizing ability, and leaching resistance was investigated.  $T_g$  of PVC plasticized with palm oil-based compound has decreased to approximately  $65 \text{ }^\circ\text{C}$  at  $20 \text{ wt}\%$  loading. Those plasticized with lower molecular weight plasticizer recorded slightly lower  $T_g$  owing to the better mobility and penetrating ability of the plasticizers to reach and accommodate the space between PVC chains. As for thermal stability, PVC



**Fig. 10** Number of eggs hatched when immersed in NaCl solution contaminated with DEHP or PLAST-A

**Fig. 11** Images of brine shrimps larvae and eggs which captured under digital microscope



blended with higher molecular weight plasticizer tend to have higher activation energy of decomposition,  $E_d$ . Plasticizer with higher molecular weight was also found to be able to retain itself better in PVC matrix. After immersed in heptane or ethanol/water solution for a week, PVC film which was plasticized with Plast-A recorded significantly lower weight loss compared to those with Plast-D or DEHP. The molecular weight of the plasticizer was also found to have effects on the mechanical properties of the PVC, where the tensile strength and elongation at break both improved with the incorporation of 10 wt% of the high molecular weight plasticizer. All these lead to the conclusion that the molecular weight of polymeric plasticizers can be manipulated to alter the properties of the PVC accordingly. The palm oil-based compound serves as an excellent plasticizer for PVC and is relatively less harmful to the environment, as evidenced in the toxicity test result.

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