

Comparison of Performance and Characteristic of Suberate, Azelate and Sebacate as PVC Plasticizers

(Perbandingan Prestasi dan Pencirian Suberat, Azelat dan Sebakat sebagai Bahan Pemplastik PVC)

NUR HAFIFAH NAHDIRAH JAFRI, NOR HAMIDAH ABU OTHMAN & MOHD. FIRDAUS MOHAMAD YUSOFF*

Chemical Science Department, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor Darul Ehsan, Malaysia

Received: 8 April 2022/Accepted: 8 January 2023

ABSTRACT

Consumer's health and safety problems that arise from using di (2-ethylhexyl) phthalate (DEHP) as a conventional plasticizer for PVC have led to the study of the production of alternative plasticizers based on dicarboxylate esters. In this study diester plasticizers based on suberic, azelaic and sebacic acid were synthesized with 2-ethylhexanol. PVC blends with these three diesters was conducted by solvent-casting technique. The characteristics of dicarboxylate esters plasticizers, which were judged to have excellent compatibility with PVC proved and evaluated by mechanical, thermal and migration stability test analyses as compared to DEHP. Improved tensile strength, elastic modulus, and elongation at break were observed in plasticized PVC films. Single peak of glass transition showed in all PVC-diester blends had lower range of temperatures, T_g (65.36 °C - 71.90 °C). The first stage of maximum degradation temperature for PVC-D2EHSu, PVC-D2EHAz and PVC-D2EHSe films were recorded at 287.06 °C, 290.83 °C and 281.68 °C, respectively, which exhibited good thermal stability. The good compatibility between synthesized plasticizers and PVC proved that the dicarboxylate plasticizers able to replace DEHP and highly capable to use as either primary or secondary plasticizers in food packaging, medical devices and domestic appliances in polymer industry.

Keywords: DEHP; diester plasticizers; polymers; PVC

ABSTRAK

Masalah kesihatan dan keselamatan pengguna yang timbul akibat daripada penggunaan di (2 etilheksil) ptalat (DEHP) sebagai pemplastik konvensional untuk polivinil klorida (PVC) telah membawa kepada kajian penghasilan pemplastik alternatif berasaskan ester dikarboksilat. Dalam kajian ini, bahan pemplastik diester berasaskan asid suberat, azelat dan sebakat telah disintesis dengan 2-etilheksanol. Adunan PVC dengan ketiga-tiga diester ini telah dilakukan dengan menggunakan teknik acuan-pelarut. Pencirian terhadap struktur, sifat mekanikal, terma dan kadar migrasi setiap pemplastik ester dalam PVC menunjukkan hasil yang baik kerana mempunyai keserasian adunan sama seperti DEHP. Ujian mekanikal filem merekodkan nilai kekuatan tegangan, tensil modulus dan panjang terikan pada takat putus yang lebih baik dalam filem PVC-diester. Puncak suhu peralihan kaca tunggal dikesan pada julat suhu yang rendah (65.36 °C - 71.90 °C). Filem PVC-diester ini menunjukkan kestabilan terma yang baik dengan suhu degradasi maksimum pertama dalam filem PVC-D2EHSu, PVC-D2EHAz dan PVC-D2EHSe masing-masing direkodkan pada 287.06 °C, 290.83 °C dan 281.68 °C. Keserasian yang baik antara pemplastik tersintesis dan molekul PVC membuktikan pemplastik diester dapat menggantikan DEHP dan berpotensi tinggi digunakan sebagai pemplastik primer atau sekunder dalam aplikasi pembungkusan makanan, peralatan perubatan dan perkakas rumah dalam sektor industri polimer.

Kata kunci: DEHP; pemplastik diester; polimer; PVC

INTRODUCTION

The worldwide production of bioplastics is about 750,000 tons/year and is very modest when compared with 300 million tons/year of conventional plastics derived from

petroleum; it is estimated that in the near decades, the growth will be exponential, reaching about 1,000,000 tons/year in 2023 as reported by Nova Institute (Rameshkumar et al. 2020). Phthalate esters has been described for more

than 80% of all the polyvinyl chloride (PVC) plasticizers due to its good performance and low price (Wang, Nie & Li 2016). Numerous studies show that the phthalate esters from the air can penetrate human skin promptly. By then, the phthalate esters plasticizers have been banned and outlawed to be marketed in the toys and childcare related which using by the children below the age of three (Czogala, Pankalla & Turczyn 2021; de Andrade Souza et al. 2021).

Natural and synthetic esters are fundamental material including acid dicarboxylic acids in the chemical industry (Gryglewicz et al. 2006). They have been most commonly potential alternative as plasticizer which ecologically friendly in polymeric formulation specifically for PVC (Coltro, Pitta & Madaleno 2013). Esters are of particular interest due to their exceptional properties, such as low volatility, high flash point, good thermal stability, and low toxicity (Gryglewicz & Oko 2005). The esters based on dicarboxylic acids (comprised of two carboxyl groups) are organic, oxygen-containing compounds, synthesized via esterification from the reaction of an alcohol. Acid and alcohol are esterified either thermally or in the presence of acid or base catalyst. PVC is characteristically plasticized in order to increase its physical properties either flexibility or workability and thus reduces glass transition (T_g) temperatures, as well as the elastic modulus in order to meet the requirements of several applications (Ahmed et al. 2021; Bocqué et al. 2016).

The present study focuses on the synthesis of esters based on medium chain acid which are suberic, azelaic and sebacic acids then reacted with 2-ethylhexanol. The research objective was to acquire an efficient, green PVC plasticizer that can be entirely or partially replace the conventional DEHP plasticizer. Therefore, different ratios of diesters and DEHP were used in PVC blends to assess their compatibility. Meanwhile, mechanical properties, thermal stability and migration stability of plasticized PVC films were evaluated and compared to DEHP plasticization efficiency. The migration resistance of the plasticizers was evaluated through chemical extraction test and exudation test to assess their use under appropriate conditions.

MATERIALS

Dicarboxylic acid, which are suberic, azelaic and sebacic acids, was procured from Aldrich Chemical. 2-ethyl-1-hexanol, sulfuric acid, sodium chloride, sodium hydrogen bicarbonate, ethyl acetate, toluene and ethanol were obtained from System and used directly without

further purification. Pure PVC resin with K value of 70 is from Aldrich Chemical. Ingredients such as DEHP, heat stabilizer of zinc stearate and stearic acids added to PVC formulation were supplied from Aldrich Chemical.

METHODS

DIESTER SYNTHESIS AND DEAN-STARK DISTILLATION SETUP

In this study, Fischer esterification of dicarboxylic acids with 2-ethyl-1-hexanol, were mixed separately at tested range of mole ratio as previous study (Jafri, Othman & Salimon 2017). In this reaction, concentrated sulfuric acid were used as a catalyst that also acts as a strong dehydrating agent. The mixture later was placed into a three-necked flask equipped with a thermometer, drop funnel, magnetic stirrer and connected with Dean-Stark apparatus. The mixture was stirred and heated at fixed temperatures, then different amount of sulfuric acid and 40-50 mL of toluene were added as an azeotropic agent as the reaction was being implemented. The esterification reaction was carried out at an optimum duration: 4 hours. Throughout the reaction, water was continuously and constantly distilled off from the system until esterification ended.

PURIFICATION OF DIESTERS

Crude product containing followed toluene was then being left to cool at room temperature before undergoing purification step using separatory funnel. The crude solution was then washed off with saturated sodium hydrogen bicarbonate, sodium chloride and ethyl acetate solvent and followed by distilled water. The purification steps were repeated more than three times until pH 7, neutral solution achieved. Thereafter, anhydrous sodium sulphate was added into ester solution and left overnight to remove water residue and evaporated. Rotary evaporator used to completely eliminate and remove traces of ethyl acetate solvent and other solvents. The yield percentage (%) of each of diester products was calculated and recorded.

CHARACTERIZATION OF DIESTER

The purities of diesters: di-2-ethylhexyl suberate (D2EHSu), di-2-ethylhexyl azelate (D2EHAz), and di-2-ethylhexyl sebacate (D2EHSe), obtained were characterized by Attenuated Total Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR), Nuclear Magnetic Resonance (^1H and ^{13}C) NMR using Bruker 400

MHz instrument using CDCl_3 as the solvent according to Aigbodion and Bakare (2005) and elemental analysis.

PREPARATION OF PVC FILMS

Five types PVC films were prepared: unplasticized PVC, plasticized PVC-D2EHSu, PVC-PVC-D2EHAz, PVC-D2EHSe, and PVC-DEHP films. Various combinations (on weight basis) were used and made as plasticizing mixtures. Four series of plasticized PVC blends were mixed and PVC/DEHP used as a reference for comparison. In each case, 40, 50 and 60 per hundred resins (phr) of this mixture was mixed with 100 parts of PVC. The different blends used for the formulation of of PVC films

are displayed in Table 1. Films prepared with different plasticizer combinations were further mixed for 24 h by using tetrahydrofuran as mutual solvent at a temperature of 60 °C to homogenize PVC blend resins (Lindström & Hakkarainen 2006). This preparation is thus called solvent-casting technique which the PVC blend was casted out to a petri dish and allowed to dry inside a fume hood for 24 h. THF solvent residue in film was removed completely by heating them inside vacuum oven at 70 °C for 48 h. These procedures were applied to prepare all plasticized PVC films with commercial plasticizers, DEHP and synthesized diesters. PVC film without plasticizer (henceforth referred to as PVC) was prepared in a similar manner to serve as the control.

TABLE 1. Compositions of the plasticized PVC films formulation

Films (phr)	Formulation number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
PVC	100	100	100	100	100	100	100	100	100	100	100	100	100
Zn stearate	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
SA	2	2	2	2	2	2	2	2	2	2	2	2	2
D2EHSu	-	40	50	60	-	-	-	-	-	-	-	-	-
D2EHAz	-	-	-	-	40	50	60	-	-	-	-	-	-
D2EHSe	-	-	-	-	-	-	-	40	50	60	-	-	-
DEHP	-	-	-	-	-	-	-	-	-	-	40	50	60

MECHANICAL TEST

Film specimens were cut and prepared according to ASTM D-638 (2007) standardization. The mechanical test parameter: tensile strength, elastic modulus and elongation at break were determined at room temperature using the universal dynamometer (INSTRON 5566, USA) at constant rate of 10 mm/min by using a 50 N load. The procedure was adapted from Xie et al. (2014) report.

THERMOGRAVIMETRY ANALYSIS (TGA)

Thermal degradation behavior analyses were conducted using a thermogravimetry analyzer TGA (TGA851 Mettler

Toledo, USA). All the film samples were evaluated from ambient to 600 °C under nitrogen flow (40 mL/min) at 10 °C/min heating rate. According to standardization ASTM E2550-17 (2017), TGA scans measure mass/weight changes in a sample and observe the rate of changes in weight based on increasing temperature and time.

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Glass transition temperature (T_g) was obtained by using differential scanning calorimetry DSC822 Mettler Toledo (TA Instruments, USA) which was calibrated with indium. Each of film samples (7-8 mg) were weighed

and conditioned in aluminum pans, then equilibrated at 25 °C and heated to 180 °C at a constant rate of 10 °C/min. The test was carried out under nitrogen flow of 50 mL/min with heating rate at 10 °C followed by ASTM D3418 (1999).

MIGRATION RESISTANCE ANALYSIS

The leaching test of chemical extraction were executed following Standard Test Method ASTM D 1239-98 (2006) procedures. PVC film specimens (60 mm × 10 mm × 2 mm) were pre-conditioned at 23 ± 2 °C with a humidity of 50 ± 5% for 24 h. Later, the specimens were immersed in 30 mL of four different solvents (petroleum ether, 10% ethanol, 30% acetic acid and distilled water) at surrounding temperature of 23 ± 2 °C for 24 h. The films were then removed from the solvent, washed meticulously with distilled water, and dried. Each specimen was repeated at least three times to calculate the average value of weight loss. Weight loss (%) = $[(W_1 - W_2)/W_1] \times 100$, where W_1 = initial weight of test specimen, and W_2 = final weight of test PVC specimen.

Exudation tests were performed according to the International Standard D2199-82 (1999) to determine the weight changes of plasticized films. PVC film specimens (60 mm × 10 mm × 2 mm) were carried out by placing a sample of PVC films between two pieces of vegetable parchment placed in a drying oven at 60 °C, for 24 h. After one day, samples were washed with distilled water and dried. Each measurement was repeated three times to record the mean value of weight loss of film. The weight loss calculation was determined using

the same equation as chemical extraction test.

RESULTS AND DISCUSSION

DIESTER SYNTHESIS

Every three different dicarboxylic acids were prepared separately by mixing it with 2-ethyl-1-hexanol at (1: 2.5) mole ratio and at other related optimum parameters. The esterification reaction procedures were set up as explained in the method section. This study was fixated on the synthesis of dicarboxylic acids with medium chain carbon length and 2-ethyl-1-hexanol and the effect of the chemical characterization of diester formed. The yield percentage (%) of diester was presented in the Table 2. The results presented that the diester yield percentage which in fact, influenced by the electrophilic character of carbonyl carbon of dicarboxylic acids, that increased as number of lengths of chain carbon decreases (Salimon et al. 2015). Figure 1 displays the esterification reaction scheme of sebacic acid and alcohol to produce D2EHSe. Table 2 also showed that D2EHSu had the highest yield percentage at 88%, whilst both D2EHAz and D2EHSe gave the same yield percentage at 87% among all diesters. The chemical structures for D2EHSu and D2EHAz were shown in Figures 2 and 3. All three diesters obtained were in high yield percentage range. The estimation molecular weight for D2EHSu, D2EHAz and D2EHSe diester were 398.63, 412.66 and 426.68 gmol^{-1} , respectively, while DEHP was 390.56 gmol^{-1} . Once diesters blended to PVC formulation, the molecular weight of films possibly in a range of 233,396 - 233,426 gmol^{-1} as the average M_w of PVC was ($\pm 233,000 \text{ gmol}^{-1}$) based on possible structure of diesters.

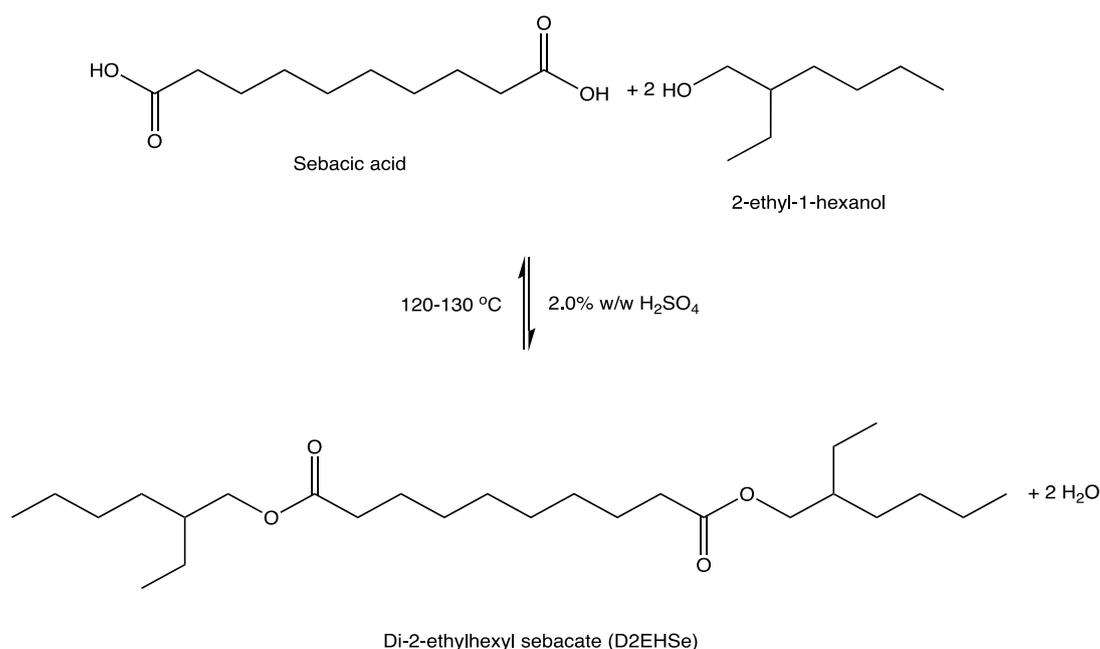
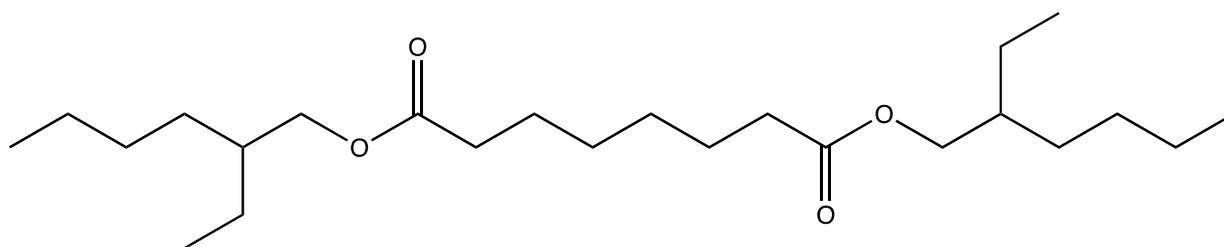
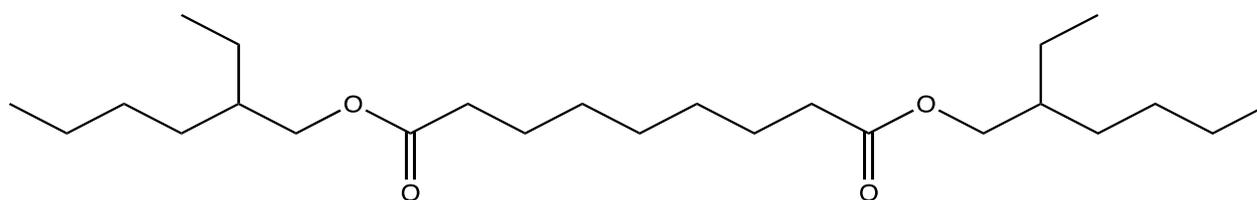


FIGURE 1. Esterification reaction of sebacic acid and alcohol to produce D2EHSe



Di-2-ethylhexyl suberate (D2EHSu)

FIGURE 2. Chemical structure of D2EHSu



Di-2-ethylhexyl azelate (D2EHAz)

FIGURE 3. Chemical structure of D2EHSu

TABLE 2. The yield percentage (%) of diesters

Diester	D2EHSu	D2EHAz	D2EHSu
Yield %	88	87	87

DIESTER SAMPLE CHARACTERIZATION

All of three dicarboxylate ester chemical structures were confirmed by FTIR, ^1H and ^{13}C NMR spectroscopy. The ATR FT-IR result provided significant peaks of carbonyl stretching vibrations ($\text{C}=\text{O}$) of ester at the range of 1735 to 1750 cm^{-1} . In this observation, hydroxyl (OH) stretching vibrations of alcohol (3230 – 3550 cm^{-1}) and the bonded hydrogen–oxygen stretching of acids (1700 – 1725 cm^{-1}) were absence in the product spectra. This insinuated that the final products of diester were free of any unreacted alcohol and acid impurities (Dyer 1965). Thus, the synthesis of diesters had complete esterification using optimized parameter reaction conditions. Bands

appearing for $-\text{CH}_3$ groups (2850 – 3000 cm^{-1}), $\text{C}-\text{O}$ stretching vibrations (1000 – 1300 cm^{-1}) and $\text{C}-\text{O}-\text{C}$ (965 – 1101 cm^{-1}) were obviously seen in the spectra. Figure 4 displayed the FTIR spectra of di-2-ethylhexyl suberate (D2EHSu) as one of the final product and suberic acid as a raw diacid. The peak of carbonyl group ($\text{C}=\text{O}$) of diacid existed at 1685 cm^{-1} , whereas at 1735 cm^{-1} for D2EHSu.

^1H and ^{13}C NMR were the most valued technique to evaluate and confirmed molecular structure of the synthesized compound. The ^1H and ^{13}C NMR results of all three synthesized diesters showed in Figures 5 and 6. Sample prepared approximately about 10 mg dissolved in 0.65 mL of deuterated chloroform (CDCl_3)

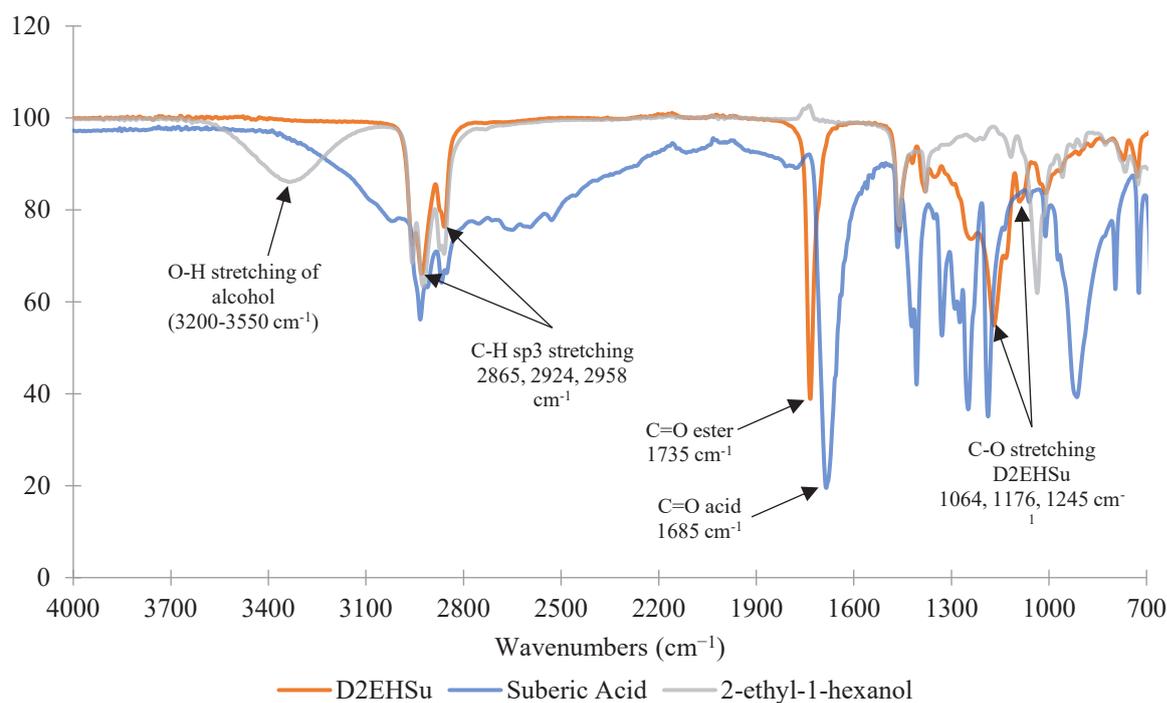


FIGURE 4. Comparison FTIR spectrum of D2EHSu, diacid and alcohol

as solvent for NMR. The chemical shifts of spectra are reported in unit of part per million (ppm). It showed the confirmation of assignment signals. The ^1H chemical shifts peaks of D2EHSu, D2EHAZ and D2EHSe were noticeably appeared at 3.92 ppm, 3.73 ppm and 3.80 ppm, respectively, for RCOO-CH_2 (d). Signal peaks of D2EHSu at 2.24 ppm for $\text{H}_2\text{C-COOR}$, 1.51 ppm for $-\text{CH}$ (3° aliphatic), 1.23 -1.29 ppm for $-\text{CH}_2-$ (saturated alkyl chain) and 0.83 ppm for $-\text{CH}_3$ (terminal methyl in alkyl chain). ^{13}C NMR spectroscopy is more understandable as all carbon items in the organic compounds give distinguishing peak signals, either they are related to protons or not was important for structural information of compound which can be found from ^{13}C NMR spectra. It is affirmed that the peak confirmation of carbonyl group is at 170-185 ppm (Pavia et al. 2014). In this case, the ^{13}C NMR results of D2EHSe in Figure 4(C) displayed the main signals of assignments. The ^{13}C chemical shift peaks of D2EHSu, D2EHAZ and D2EHSe was shown at 173.75 ppm, 173.10 ppm, and 172.96 ppm, respectively, for (C=O) of ester group. Meanwhile, the signal peaks of D2EHSe at 65.94 ppm for (O-C) ester, 33.61 ppm for ($\text{CH}_2\text{-C=O}$) ester, 38.56 ppm for ($-\text{CH}$ (3° aliphatic)), 24.74-30.05 ppm for $-\text{CH}_2$ (saturated alkyl chain), then

24.55 and 24.61 ppm for CH_3 (terminal in alkyl chain).

Elemental analysis was verified by using CHNS/O Thermo Fischer Scientific FLS0002 elemental analyser. Sample solution were homogenized using vortex first and prepared approximately about 8-10 mL of solution then introduced to the vials. The close similarities between experimental and theoretical analysis data corroborate the purity of the final diesters. The comparison of experimental and theoretical analysis data is given in Table 3 for D2EHG, D2EHSu and D2EHSe diesters. The validation of empirical formula of D2EHAZ as an example was calculated by the mole ratios of C and H. As the practical content of C (72.87%) and H (11.74%), the calculated mole ratios were 6.31 and 12.11 individually, which gave the empirical formula of D2EHG ($\text{C}_{6.31}\text{H}_{12.11}$). It was very closed to the theoretical empirical formula ($\text{C}_{6.25}\text{H}_{12}$).

MECHANICAL PROPERTIES OF FILMS

The mechanical test of the PVC and all plasticized PVC films were performed to determine tensile strength, elastic modulus and elongation at break. Mostly, the plasticizers help in improving the plastic material's flexibility and

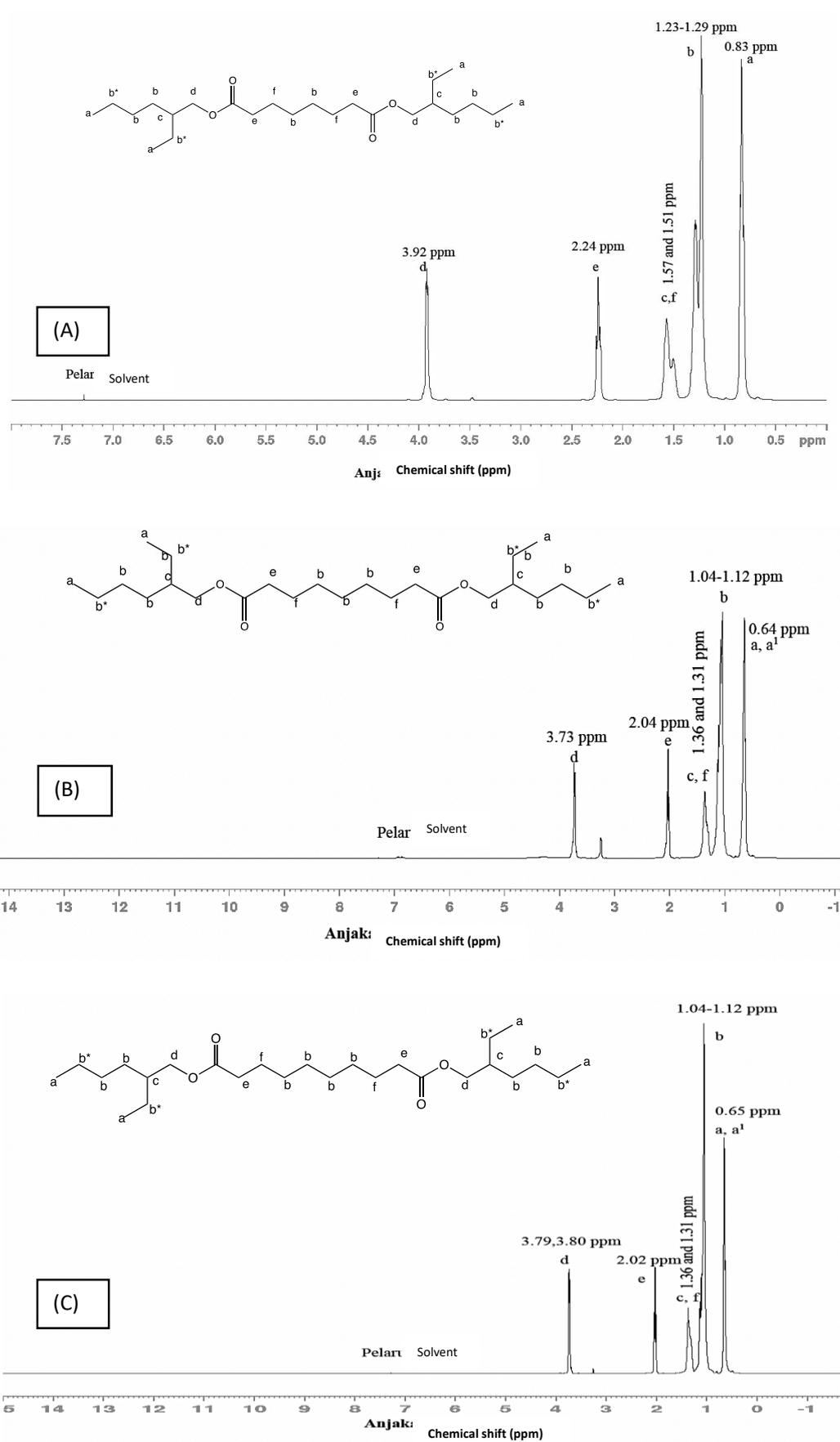


FIGURE 5. ^1H NMR spectrum of diesters: (A) D2EHSu, (B) D2EHAz and (C) D2EHSe

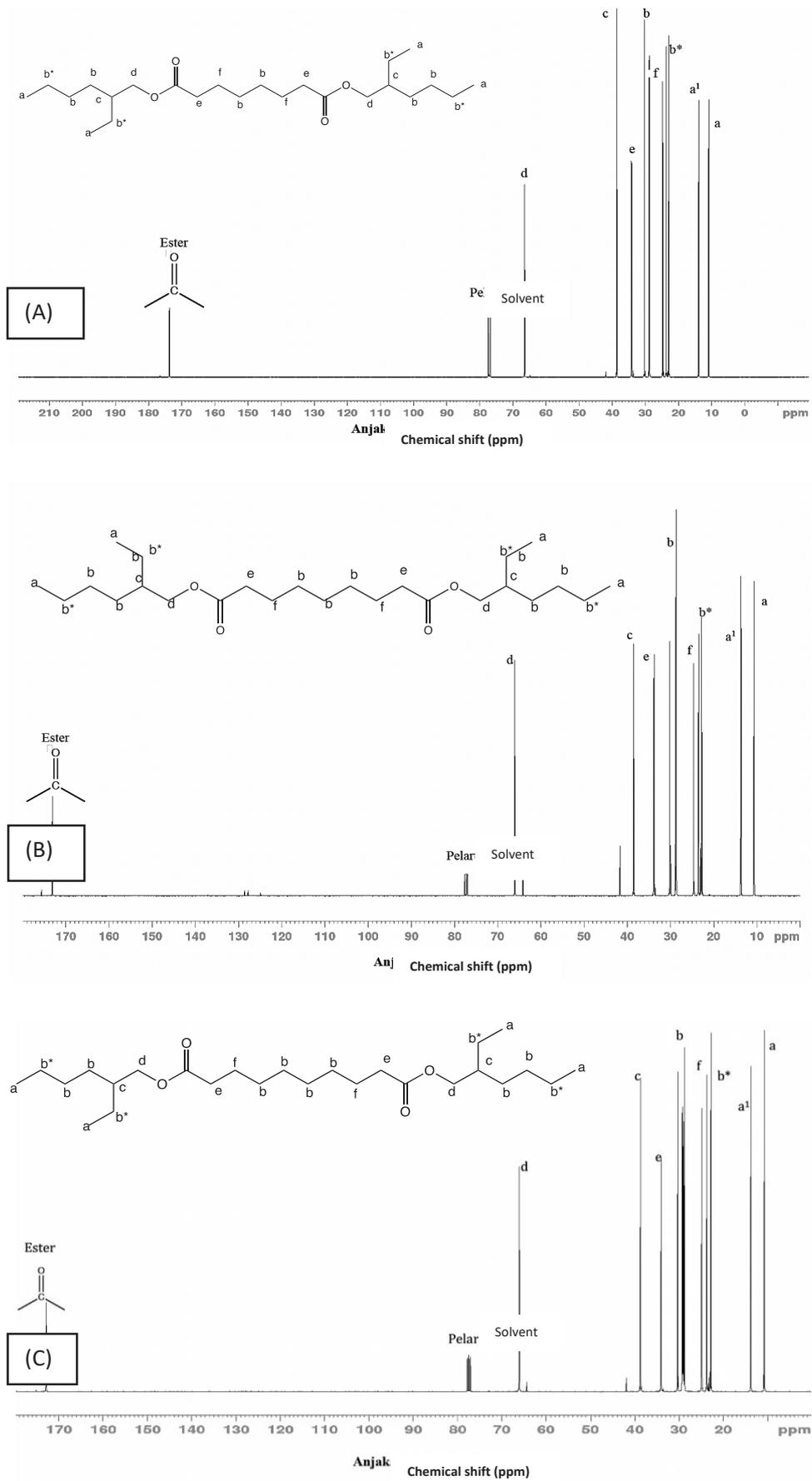


FIGURE 6. ^{13}C NMR spectrum of diesters: (A) D2EHSu, (B) D2EHaz and (C) D2EHSe

TABLE 3. Elemental analysis of C and H content of diesters

Dicarboxylate	Empirical formula	Experimental content		Empirical formula	Theoretical content	
esters	of ester (Experimental)	of C, H (100%)		ester (theory)	of C, H (100%)	
		C	H		C	H
D2EHSu	$C_{5.97}H_{11.50}$	71.93	11.60	$C_{5.96}H_{11.43}$	72.31	11.63
$C_{24}H_{46}O_4$						
D2EHAz	$C_{6.31}H_{12.11}$	72.87	11.74	$C_{6.25}H_{12}$	72.77	11.73
$C_{25}H_{48}O_4$						
D2EHSe	$C_{6.56}H_{12.26}$	73.54	11.53	$C_{6.5}H_{12.5}$	73.19	11.81
$C_{26}H_{50}O_4$						

elongation by weakening the interchain polymer-polymer interactions. As presented in Figure 7, as diester content increased, the tensile strength of the blends also increased as compared from 6.798 MPa unplasticized (PVC) to 6.330 MPa (DEHP), 8.567 MPa (D2EHSu), 12.692 MPa (D2EHAz) and 13.961 MPa (D2EHSe) at 40 phr. Then, all films showed significant decrease value in tensile strength as more plasticizer added to PVC blends which indicates that the addition of diesters significantly enhanced the flexibility properties of PVC matrix. This might be because of the domination of strong hydrogen bonds produced by PVC-plasticizer intermolecular interaction over PVC-PVC attraction. This could be suggesting that the alkyl chains in diesters might be influenced and balanced with that of the rigidity groups of PVC as diesters were added in resin to achieve better film flexibility. The result also coherent with the Bargellini's investigation, which explained that tensile strength is related to the magnitude of the plasticizer's polarity and the plasticizer's amount (Daniels 2009). According to Yu et al. (2013), ester product prepared from glycerol, acetic acid, and benzoic acid gave higher tensile strength and hardness than DEHP.

Elastic modulus of the PVC blends boosted from 11.360 MPa unplasticized (PVC) to 97.704 MPa (DEHP), 108.505 MPa (D2EHSu), 152.891 MPa (D2EHAz) and 371.812 MPa (D2EHSe) for plasticized films as presented in Figure 8. The value then fluctuates immediately as the concentration increased from 40 phr to 60 phr, regardless of plasticizer type. It is perceived that the modulus of elasticity declines with increasing

plasticizer content up to certain level in PVC films. Both modulus of elasticity and tensile strength value decreasing probably because, the bond force of the polymer atoms become weaker due to the linked interaction and thus free volume increases with the addition of the plasticizer to the PVC (Saunders 1973). Based on the results for the tensile strength and elastic modulus, we could explain that all of the plasticized PVC film blends at 50 phr experienced an anti-plasticization behavior because diester used exceeds the optimum concentration required. The secondary bonds formation, such as hydrogen bonds and van der Waal's interactions, between the molecules of the PVC-diester cause the anti-plasticization behavior to happen (Zhang & Rempel 2012).

Meanwhile, Figure 9 displayed elongation at break of the three different blends types of diesters were increased a little than that of unplasticized PVC (158%), unlike DEHP which had the lowest value. As the concentration of diesters was added to 50 phr, the PVC films did change from rigid to flexible film which had the highest value of 164% for PVC-D2EHSe film. Reversibly, if the plasticizers exhibit low polarity, the film blends would be immiscible with PVC to mix. A plasticizer molecule which generally had polar moieties (ester groups) that could interact with the PVC chains to ensure the resin compatibility. Moreover, non-polar groups (alkyl chains) of plasticizer then break up the chain-chain interactions and ensuing plasticizing effect (Erythropel 2016). Thus, it is significance mentioning that all of tensile properties of PVC films were improved

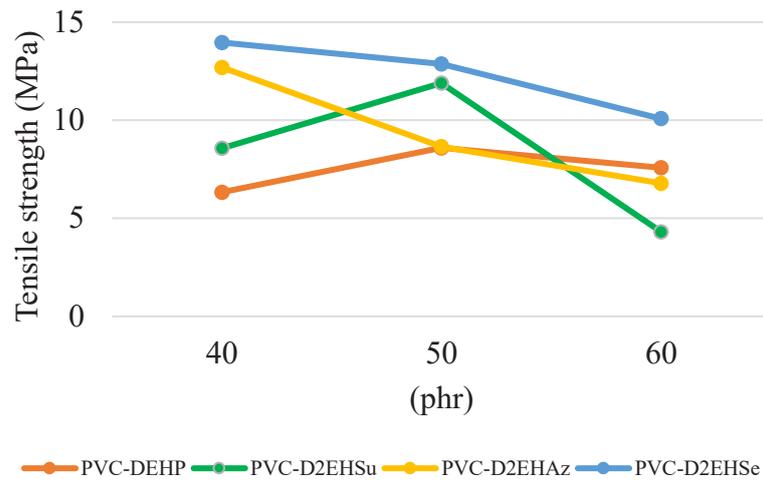


FIGURE 7. Effects of different blends of diester plasticizers on the tensile strength

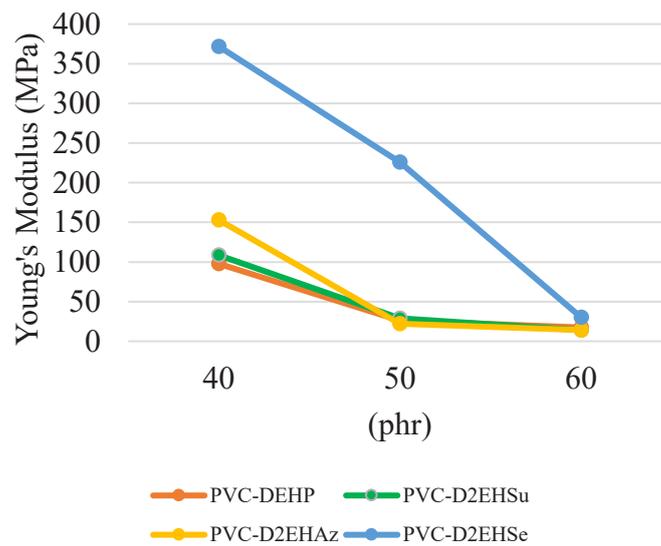


FIGURE 8. Effects of different blends of diester plasticizers on the elastic modulus

or similar to the commercial DEHP plasticizer as the diester plasticizers added. Furthermore, the result relates to film with branched ester plasticizers gave an improved mechanical properties (higher elongation at break) value than linear ester plasticizer.

GLASS TRANSITION

Glass transition temperature (T_g) is considered as one of

the most critical thermophysical transitions for modified films in plastic materials. The T_g values of the plasticized films with diesters and DEHP were conducted via DSC analysis listed in Table 4. T_g for unplasticized PVC film (F1) obtained at 72.56 °C. The DSC curves illustrated in Figure 10 explain that all diester plasticizers were effective at reducing the T_g values of all of the film blends. Generally, lowering T_g was deemed as the

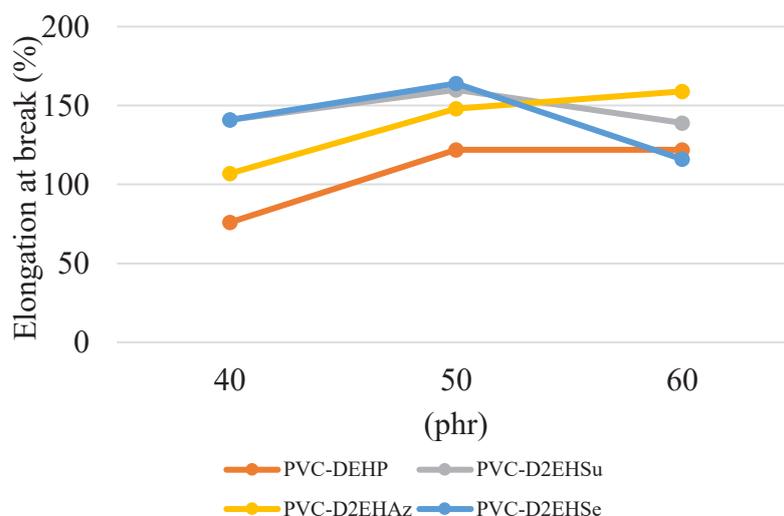


FIGURE 9. Effects of different blends of diester plasticizers on the elongation at break

plasticization of the polymeric material and dependent on the capability of plasticizers (Faria-Machado et al. 2013). In this case, all D2EHSu films: (F4 < F2 < F3: 65.36 °C < 67.05 °C < 68.40 °C) had the lowest T_g values compared to other diester blends and also lower than that DEHP film blends. It also can be seen that as the amount of plasticizer increased to 60 phr in PVC blend, every

four kinds of plasticizers showed the lowest value of T_g except PVC-D2EHAz films. This can be explained by the addition of the plasticizer would increase the movement of the molecules of polymer, then increase the polymer-polymer bonds and interaction resulting in the decrease of T_g (Wypych 2004). Hence, all diesters demonstrate an excellent plasticizing effect of plasticizers in PVC which had high potential to replace DEHP plasticizer.

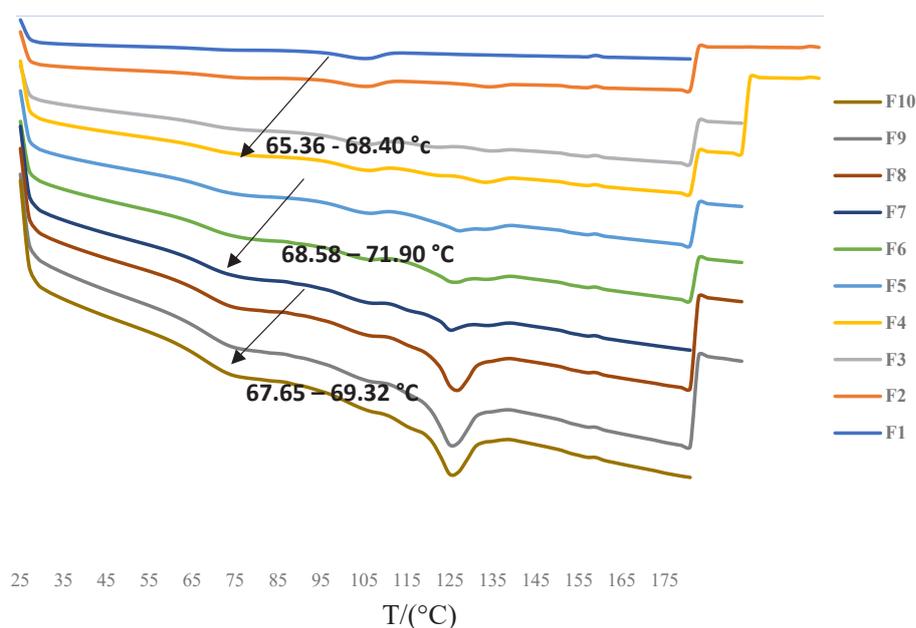


FIGURE 10. Effects of different content of diester plasticizers on the glass-transition behaviour of PVC films via DSC

THERMAL STABILITY

All the film blends were tested to thermogravimetric analysis (TGA). The data evaluation explained the effect of diesters in context of thermal stability and thermal behavior which then being compared to PVC-DEHP films. The TGA thermogram of the plasticized films were presented in Figure 11. Based on the TGA curve, two-stage of thermal degradation process occurrence were observed. The first stage was at 250 - 310 °C for diester blends while DEHP blends at 160 - 275 °C, that was corresponding to the dehydrochlorination of PVC including the formation and stoichiometric elimination of HCl.

It can be seen in the unplasticized PVC film (F1) had the first degradation at a low-temperature, 192.26 °C and molecular dehydrochlorination happen during this stage. HCl presence then formed further catalysis in the degradation process by releasing more of HCl and polyenes formation occurs (Bouchareb & Benaniba 2008). The total mass loss of diester F2-F10 films was found to be in the range (68.70-70.66%) between 281.68 °C and 320.11 °C in the first maximum decomposition stage. Meanwhile, the result for DEHP, F11-F13 films had their first total mass loss a slightly higher than that synthesized diester PVC films in the range (70.70 -

79.20%) between 237.33 °C and 267.90 °C. Three films which are F6, F10, and F12 only went through one stage of degradation. So, the first mass loss represented loss of chlorine as HCl and also loss of plasticizer system or its decomposition products.

The second stage degradation of F1 film occurs at 385.65 °C, whereas the onset temperature range for PVC-diester blends were at 379 - 455 °C and PVC-DEHP blends was at 363 - 376 °C. Throughout the thermal decomposition, the degradation of complex structure such as the cross linking, cyclization, splitting of chains, and aromatization happens (Pitchaimari et al. 2014). The second total mass loss of diester F2-F10 films was observed in the range 10.94% - 17.40% that occurs between 462.41 °C and 471.51 °C. Overall, the decomposition temperatures observed were higher as the amount of diester incorporated in PVC formulation blend increased for the first step of dehydrochlorination stage. The values of initial degradation temperatures, maximum degradation temperature and weight loss are summarized in Table 4. It was concluded that the plasticizer incorporation affects the thermal stability of the PVC films. PVC-D2EHSu film (F2) is the most effective in thermal stability due to having 81.75% total weight loss and had better tendency to substitute DEHP in PVC formulation.

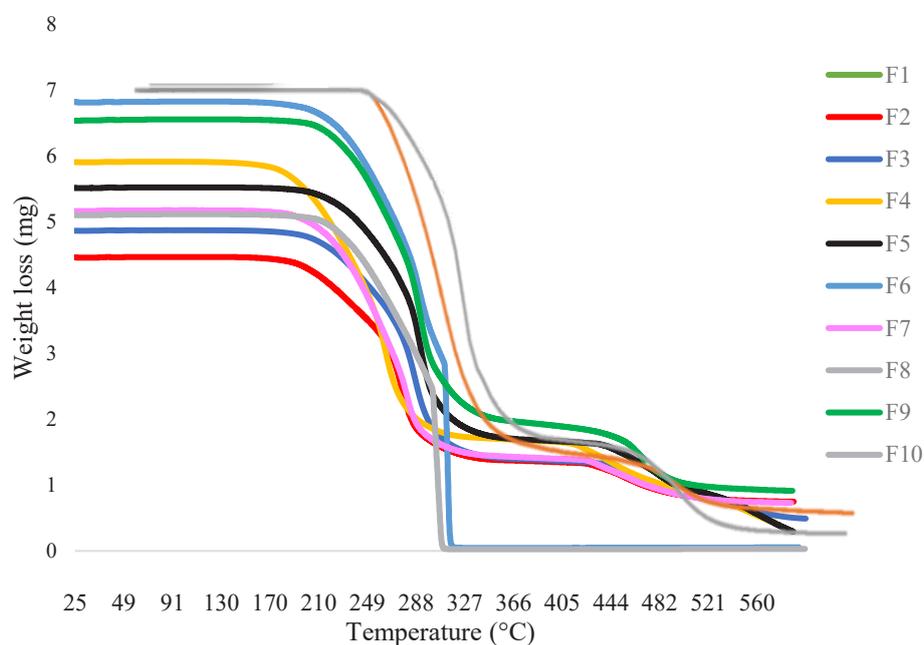


FIGURE 11. Effects of different diester plasticizers concentration on the thermal stability of PVC films via TGA thermograms

TABLE 4. Thermal properties of PVC-Diester blends and PVC-DEHP

FILMS	T _G (°C)	1 ST STAGE (°C)			2 ND STAGE		
		T _D ^A (°C)	T _{MAX} ^B (°C)	% WEIGHT LOSS	T _D ^A (°C)	T _{MAX} ^B (°C)	% WEIGHT LOSS
F1	72.56	192.26	262.71	69.38	385.65	460.74	9.85
F2	67.05	261.15	287.06	68.84	443.25	465.17	12.91
F3	68.40	260.38	288.35	70.66	443.65	466.22	10.94
F4	65.36	256.70	289.13	70.54	442.09	471.51	12.05
F5	68.58	267.41	290.83	68.70	449.33	483.77	12.67
F6	71.52	310.91	320.11	99.24	-	-	-
F7	71.90	306.13	293.10	69.29	449.96	473.16	13.59
F8	68.19	213.50	281.68	65.78	379.48	462.41	17.40
F9	69.32	265.69	295.09	69.29	455.60	471.25	13.59
F10	67.65	292.91	304.43	99.67	-	-	-
F11	69.15	167.64	237.33	70.70	362.65	456.47	12.90
F12	69.65	222.74	275.74	98.00	-	-	-
F13	69.01	177.59	267.90	79.20	376.44	465.20	12.28

^a The onset degradation temperature. ^b Temperature at maximum weight loss

CHEMICAL EXTRACTION AND EXUDATION RESISTANCE
Plastics are considered to be chemically inert but the migration of substances from plastics into products is well known. Hence, the use of plastics in contact with products must be controlled by the identification of migrating compounds using chemical extraction method. Migration

is mostly due to the low solubility of the compounds in the polymer and is also known as leaching (Schwach & Vert 1999). The arrangement amount of weight changes order was as follows: petroleum ether, 10% ethanol, 30% acetic acid and water resulted from each film as displayed in Table 5. The results indicated that the plasticized PVC

TABLE 5. Degree of plasticizer migration after chemical extraction test

Films	(±) Weight changes (%)			
	Distilled water	Ethanol 10%	Acetic acid 30%	Petroleum Ether
F1	0.15	0.35	0.33	-43.37
F2	-0.23	0.00	-0.51	-19.03
F3	-0.43	-1.90	-1.00	-29.72
F4	0.00	0.00	-0.26	-35.53
F5	-0.68	-0.73	-0.34	-16.09
F6	0.00	-1.41	-0.62	-37.15
F7	-0.99	-0.80	0.00	-36.88
F8	-1.29	-0.15	-0.32	-27.35
F9	0.00	0.00	-0.68	-32.98
F10	-0.71	-0.40	-0.18	-35.93
F11	0.00	0.00	-0.41	-46.84
F12	0.34	-0.18	-1.10	-45.57
F13	0.00	-0.26	1.00	-38.86

had no significant weight loss (less than 2.0%) in aqueous environment. As a comparison, the weight loss of PVC-DEHP films and PVC-Diester decreased gradually as the mass ratio of plasticizer in the PVC samples increased especially in petroleum ether solution. However, all (F2-F10) synthesized diester PVC films still had lower weight loss than commercial PVC-DEHP (F11-F13) films. These results could be proving that the stronger intermolecular interaction between the PVC and the diester plasticizers resulting better compatibility. In addition, it was also mentioned plasticizer migrated out of liquid or a solid, branched plasticizers reported to have

less plasticizer loss than linear plasticizers (Czogala, Pankalla & Tureczyn 2021).

Figure 12 showed exudation properties of diesters PVC films with different concentration and type. The most notably that had the highest exudation resistance was PVC-D2EHSu (F3 < F2 < F4) films with range of 0.25 - 0.35 %. This may explain that D2EHSu had stronger intermolecular forces between the PVC chain and D2EHSu molecule. In summary, the amount of exudation loss of all films during experimental duration is less than 1.0%, implying that all of the plasticizers were fully compatible with PVC and could not be easily extracted out of PVC matrix.

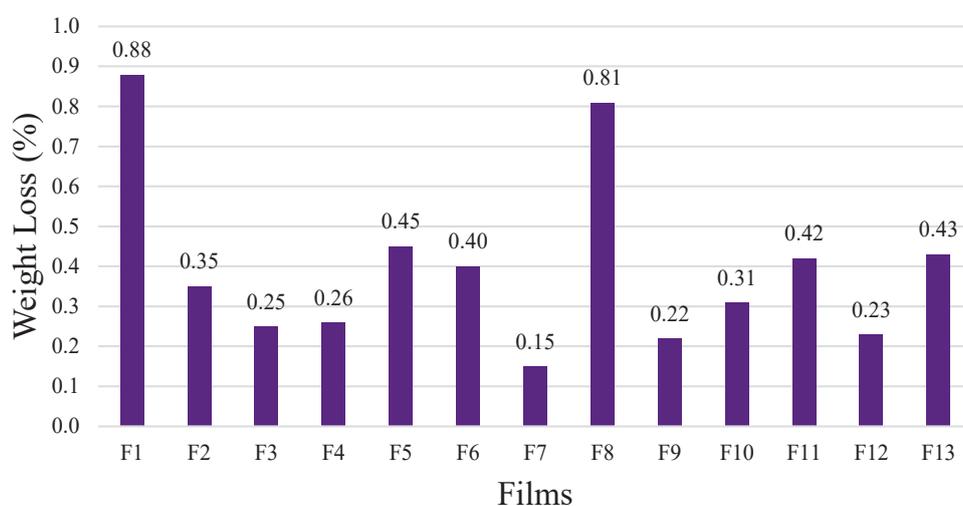


FIGURE 12. Degree of plasticizer migration after exudation test

CONCLUSIONS

Three types of diesters (D2EHSu, D2EHAz, and D2EHSe) were synthesized and incorporated with PVC resin using an environmentally friendly method. Mechanical properties on PVC films plasticized with the dicarboxylate esters indicated that flexible PVC were attained the best when diester concentrations was 50 phr. The result showed that the tensile strength and elastic modulus decrease while elongation at break increased, which found to be improved than those of PVC plasticized with the same amount of DEHP. The glass transition temperature (T_g) and thermal degradation of all of the plasticizers were found to be lower than unplasticized PVC. Particularly, the degradation occurred in two stages which elaborate the thermal behavior of the films. Furthermore, the leaching test of the PVC films

mixed with three diester plasticizers showed that the use of a lower content of plasticizers provide better migration resistance when examined in different contacting solvent medium. Moreover, all the result from analysis signified that all of the plasticizers had good compatibility and miscible with PVC resin that also highly prospective to substitute DEHP applications in commercial uses.

ACKNOWLEDGEMENTS

The authors would like to thank the Chemical Science Department, Faculty of Science and Technology, Universiti Kebangsaan Malaysia for instrumental facilities as well as grants for funding the project FRGS/2/2014/ST01/UKM/01/2, GUP-2016-012 and the Ministry of Education, Malaysia.

REFERENCES

- ASTM E2550-17. 2017. *Standard Test Method for Thermal Stability by Thermogravimetry*. ASTM International, USA, West Conshohocken, PA.
- ASTM D638-14. 2016. *Standard Practice for Preparation of Metallographic Specimens*. ASTM International, USA, West Conshohocken, PA.
- ASTM D2199-82. 1999. *Standard Test Method for Measurement of Plasticizer Migration from Vinyl Fabrics to Lacquers*. ASTM International, USA, West Conshohocken, PA.
- ASTM D1239-98. 2006. *Standard Test Method for Resistance of Plastic Films to Extraction by Chemicals*. ASTM International, USA, West Conshohocken, PA.
- Ahmed, W.A., Yousif, E., Al-Mashhadani, M.H., Yarmo, M.A., Salih, N. & Salimon, J. 2021. The effect of long-chain and branched alcohol on lubricity of dodecanedioic acid-based ester. *Kemija u industriji* 70(1-2): 13-22.
- Aigbodion, A.I. & Bakare, I.O. 2005. Rubber seed oil quality assessment and authentication. *Journal of the American Oil Chemists' Society* 82(7): 465-469.
- Bocqué, M., Voirin, C., Lapinte, V., Caillol, S. & Robin, J.J. 2016. Petro-based and bio-based plasticizers: Chemical structures to plasticizing properties. *Journal of Polymer Science, Part A: Polymer Chemistry* 54(1): 11-33.
- Bouchareb, B. & Benaniba, M.T. 2008. Effects of epoxidized sunflower oil on the mechanical and dynamical analysis of the plasticized poly(vinyl chloride). *Journal of Applied Polymer Science* 107(6): 3442-3450.
- Coltro, L., Pitta, J.B. & Madaleno, E. 2013. Performance evaluation of new plasticizers for stretch PVC films. *Polymer Testing* 32(2): 272-278.
- Czogala, J., Pankalla, E. & Turczyn, R. 2021. Recent attempts in the design of efficient PVC plasticizers with reduced migration. *Materials* 14(4): 844.
- Daniels, P.H. 2009. A brief overview of theories of PVC plasticization and methods used to evaluate PVC-plasticizer interaction. *Journal of Vinyl and Additive Technology* 15(4): 219-223.
- de Andrade Souza, L., Francisquetti, E.L., Dalagnol, R.D., Roman Junior, C., Schanz, M.T.G., Maier, M.E. & Petzhold, C.L. 2021. PVC plasticizer from trimethylolpropane trioleate: synthesis, properties, and application. *Polimeros* 31(2): 1-10.
- Dyer, J.R. 1965. *Applications of Absorption Spectroscopy of Organic Compounds*. USA: Prentice-Hall.
- Erythropel, H. 2016. *Evaluation of Maleate, Fumarate, and Succinate Diesters as Potential Green Plasticizers*. McGill University.
- Faria-Machado, A.F., da Silva, M.A., Vieira, M.G.A. & Beppu, M.M. 2013. Epoxidation of modified natural plasticizer obtained from rice fatty acids and application on polyvinylchloride films. *Journal of Applied Polymer Science* 127(5): 3543-3549.
- Gryglewicz, S. & Oko, F.A. 2005. Dicarboxylic acid esters as components of modern synthetic oils. *Industrial Lubrication and Tribology* 57(3): 128-132.
- Gryglewicz, S., Stankiewicz, M., Oko, F.A. & Surawska, I. 2006. Esters of dicarboxylic acids as additives for lubricating oils. *Tribology International* 39(6): 560-564.
- Jafri, N.H.N., Othman, N.H.A. & Salimon, J. 2018. Optimization of esterification of dicarboxylic acids and 2-ethyl-1-hexanol. *AIP Conference Proceedings*. p. 020086.
- Lindström, A. & Hakkarainen, M. 2006. Environmentally friendly plasticizers for poly(vinyl chloride) - Improved mechanical properties and compatibility by using branched poly(butylene adipate) as a polymeric plasticizer. *Journal of Applied Polymer Science* 100(3): 2180-2188.
- Pavia, D.L., Lampman, G.M., Kriz, G.S. & Vyvyan, J.A. 2014. *Introduction to Spectroscopy*. 5th ed. United States of America: Cengage Learning.
- Pitchaimari, G., Sarma, K.S.S., Varshney, L. & Vijayakumar, C.T. 2014. Influence of the reactive diluent on electron beam curable functionalized N-(4-hydroxyl phenyl) maleimide derivatives - Studies on thermal degradation kinetics using model free approach. *Thermochimica Acta* 597: 8-18.
- Rameshkumar, S., Shaiju, P., O'Connor, K.E. & Ramesh Babu, P. 2020. Bio-based and biodegradable polymers - State-of-the-art, challenges and emerging trends. *Current Opinion in Green and Sustainable Chemistry* 21: 75-81.
- Salimon, J., Ahmed, W.A., Salih, N., Yarmo, M.A. & Derawi, D. 2015. Lubricity and tribological properties of dicarboxylic acid and oleyl alcohol based esters. *Sains Malaysiana* 44(3): 405-412.
- Saunders, K.J. 1973. *Polyesters*. *Organic Polymer Chemistry*. Springer Netherlands: Dordrecht.
- Schwach, G. & Vert, M. 1999. *In vitro* and *in vivo* degradation of lactic acid-based interference screws used in cruciate ligament reconstruction. *International Journal of Biological Macromolecules* 25(1-3): 283-291.
- Wang, Y., Nie, X. & Li, X. 2016. Synthesis and characterization of novel pentaerythritol ester as PVC plasticizer. *Journal of Applied Polymer Science* 133(47): 1-7.
- Wypych, G. 2004. *Handbook of Plasticizers*. ChemTec Publishing.
- Xie, Z., Chen, Y., Wang, C., Liu, Y., Chu, F. & Jin, L. 2014. Effects of bio-based plasticizers on mechanical and thermal properties of PVC/wood flour composites. *BioResources* 9(4): 7389-7402.
- Zhang, Y. & Rempel, C. 2012. Retrogradation and antiplasticization of thermoplastic starch. *Thermoplastic Elastomers*. InTech.

*Corresponding author; email: fir_my@ukm.edu.my