EFFECTS OF PLASTICISER MIXTURES ON PHYSICAL AND MECHANICAL PROPERTIES OF MEDICAL GRADE POLYVINYL CHLORIDE (PVC)

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MOK WEN RU

A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering

Faculty of Engineering and Science
Universiti Tunku Abdul Rahman

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **EFFECTS OF PLASTICISER MIXTURES ON PHYSICAL AND MECHANICAL PROPERTIES OF MEDICAL GRADE POLYVINYL CHLORIDE (PVC)** was prepared by **MOK WEN RU** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

Polyvinyl chloride (PVC) has been widely used in manufacturing of disposal, pre-sterilized medical device such as urine bag and urinary tubing due to its flexibility, durability, transparency, sterilization performance, and low cost. Plasticiser typically di-2-etylhexyl phthalate (DEHP) is normally incorporated into PVC resins to increase the flexibility. However, the migration tendency and toxicity of DEHP has led to gradual shift of plasticiser to high molecular weight phthalate or other alternative plasticisers. The effect of different plasticiser mixtures (mixture of dioctyl adipate (DOA) with epoxidised soybean oil (ESO), mixture of diisononyl phthalate (DINP), DOA and ESO and mixture of dioctyl terephthalate (DOTP) with ESO) and different plasticiser concentration on physical as well as mechanical properties of PVC compounds were investigated. PVC resins and additives were compounded by two roll mill machine and compression moulded with hot press machine. The physical and mechanical properties of PVC compounds were examined by conducting tensile test, hardness test, specific gravity test and scanning electron microscopy (SEM). As the plasticisers’ concentration increased, the tensile strength, Durometer hardness and specific gravity of PVC compound decreased while elongation at break increased. Besides that, among three plasticiser mixtures investigated in this study, the combination of DOA and ESO showed highest plasticising efficiency in tensile strength and Durometer hardness but lowest compatibility with PVC resins. The increment on elongation at break was also high but only limited to low plasticiser concentration. On the other hand, PVC compound plasticised with DINP, DOA and ESO posed intermediate tensile strength, Durometer hardness and compatibility. The elongation at break for this combination was lower than DOA and ESO filled PVC compounds at low plasticiser concentration (< 60 phr) but became higher when the plasticiser loading level exceeded 60 phr. Lastly, combination of DOTP and ESO showed poorest plasticising efficiency in mechanical properties including tensile strength, elongation at break and Durometer hardness but highest compatibility with PVC resins.

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LIST OF SYMBOLS/ ABBREVIATIONS

wt%	Weight percent
ATBC	Acetyl tributyl citrate
ATHC	Acetyl trihexyl citrate
BTHC	Butyryl trihexyl citrate
Ca/Zn	Calcium/ Zinc stearate
DBA	Dibutyl adipate
DBP	Di-n-butyl phthalate
DEHA/ DOA	Di-2-ethylhexyl adipate/ Dioctyl adipate
DEHP	Diethylhexyl phthalate
DEHTP/DOTP	Di(2-ethylhexyl) terephthalate/ Dioctyl terephthalate
DIDA	Diisodecyl adipate
DIDP	Diisodecyl phthalate
DINA	Diisononyl adipate
DINCH	Di-isononyl-1,2-dicarboxylate
DINP	Diisononyl phthalate
EBS	Ethylene bis-stearamide
ELO	Epoxidised linseed oil
ESO	Epoxidised soybean oil
HPLC	Hyperbranch poly(ε-caprolactone)
IUPAC	International Union of Pure and Applied Chemistry
MEHP	Monoethylhexyl phthalate
PACVD	Plasma-assisted chemical vapour deposition
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofuran
PHR	Part per hundred resin

PVC	Polyvinyl chloride
SEM	Scanning electron microscopy
SF	Substitution factor
SG	Specific gravity
TBC	Tributyl citrate
TEHTM/TOTM	Tri-2-ethylhexyl trimellitate/ Trioctyl trimellitate
TMA	Trimellitic anhydride
TMC	Trimethyl citrate
TMTM	Trimetyl trimellitate
VCM	Vinyl chloride monomer
WHO	World Health Organization

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CHAPTER 1

INTRODUCTION

1.1 Background

Polyvinyl chloride (PVC) is a thermoplastic polymer produced from polymerization of vinyl chloride monomer (VCM) which can be obtained by hydrochlorination of acetylene or thermal cracking of ethylene dichloride. It is rated as the second most produced commodity plastic after polyethylene in plastic industry (Gil et al., 2006). PVC can be polymerized through suspension, emulsion and mass polymerization where different method produces polymer with different properties and applications. The resulting PVC normally contains less than 1 ppm of VCM as regulated by the British Pharmacopeia 2010.

Unmodified PVC produced from polymerization has low commercial value due to its brittleness and rigidity at ambient temperature. Besides that, severe degradation of polymer during processing at elevated temperature and pressure shows that it has low process ability. Thus, raw PVC is normally compounded with additives such as plasticiser, stabiliser, lubricant, filler, flame retardants and other processing aids to enhance properties, improve processing characteristic and reduce cost. With the benefit of low cost, high performance, versatility, wide availability and long service life, PVC is indeed an ideal material for wide range of applications including buildings, transportation, food packaging, toys and medical devices (Louis, 2009).

PVC has been used in medical device manufacturing since 1950s to replace glass and natural rubber. The flexibility, durability, transparency, chemical stability, low toxicity, biocompatibility, sterilization performance, ease of fabrication and low cost of PVC has led to domination of this material in disposable, pre-sterilized medical devices production. Urine bag and urinary tubing are examples of disposable medical devices that are used to empty the bladder of post operation patients or those suffering from urine retention intermittently. They are frequently used due to the reduce risk of infection and ease of handling (Hakan et al., 2008).

Since flexibility is one of the major concerns of urine bag and urinary tubing, the selection and composition of plasticisers in PVC is very essential. Plasticisers are the largest volume additive used in PVC and serves to soften PVC and increase flexibility. There are more than three hundred different types of plasticisers in the world with approximately one hundred types are commercially available. Currently, the most commonly used plasticisers are phthalates, especially di-2-ethylhexyl phthalate (DEHP) due to its high plasticising efficiency, wide availability and low cost. However, the toxicity issue of DEHP has led to gradual shift of plasticiser to high molecular weight phthalate including diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP) and other alternatives such as adipates, citrates, epoxies, terephthalates, trimellitates, diisononylcyclohexane-1,2-dicarboxylate (DINCH) and phosphate esters polymerics (Markarian, 2007). The VinylPlus programme by European PVC industry also set a new target to evolve the use of plasticiser towards high molecular weight phthalates by 2020 (Ertl, 2011).

1.2 Problem Statement

To produce urine bag and urinary tubing, flexibility of material is crucial. Thus, plasticising becomes a vast subject in PVC due to the nature of raw PVC that is rigid at ambient temperature. Most of the previous studies concentrate on application of single type plasticiser which has limited application and is very different from real industrial formulation. Therefore, effects of plasticiser mixtures on mechanical and physical properties of PVC compound are worth to be studied. However, different combination and concentration of plasticisers would offer different plasticising efficiency. In order to overcome this, following problems were identified:

1. What is the effect of different plasticiser mixtures (mixture of dioctyl adipate (DOA) with epoxidised soybean oil (ESO), mixture of diisononyl phthalate (DINP), DOA and ESO and mixture of dioctyl terephthalate (DOTP) with ESO) on mechanical and physical properties of plasticised PVC blends?

2. What is the effect of different concentration of plasticisers in the plasticiser mixtures on mechanical and physical properties of plasticised PVC blends?

1.3 Objectives

The main objective of this study was to investigate optimum combination of DINP, DOTP, DOA and ESO plasticisers in PVC compound for medical grade urine bag and urinary tubing manufacturing.

In order to achieve the main objective, several specific objectives were identified as follow:

1. To investigate the effect of different plasticiser mixtures on PVC mechanical and physical properties of plasticised PVC blends.

2. To investigate the different concentration of plasticisers in the plasticiser mixtures on mechanical properties and physical properties of plasticised PVC blends.

3. To determine the most suitable combination of plasticisers and concentration of plasticiser mixture that provides optimum physical and mechanical properties.

1.4 Scope of Study

To achieve the objectives of this study, the following scopes have been carried out:

(1) Sample preparation:

- PVC resins and additives such as plasticisers, heat stabiliser and lubricant were dry blended by high speed mixer.

- The dry blends were then compounded with two roll mill machine and compressed into desired shape and thickness through compression moulding.

(2) Characterization Testing:

- Tensile Test: The tensile strength and elongation at break of PVC was tested with Shimadzu Universal Testing Machine in accordance to ASTM D 638.

- Hardness Test: The hardness of PVC was measured with Omnipotent Instruments Hardness Tester in accordance to ASTM D 2240 Type A.

- Specific gravity: The specific gravity of PVC was measured with Matsuttaku Electronic Densimeter MH – 300E in accordance to ASTM D 792 Method A.

- Scanning electron microscopy (SEM): The morphology of PVC was scanned with Hitachi S-3400N scanning electron microscope.

CHAPTER 2

LITERATURE REVIEW

2.1 Plasticisers

Suspension polyvinyl chloride (PVC) is a semi-crystalline polymer with relatively high tensile modulus which can be reduced by incorporating plasticisers into it. For semi-rigid and flexible application, PVC resins range from medium to high molecular weight with sufficient porosity is used to absorb plasticisers to achieve the desired flexibility of intended end-product (William, 2005). Plasticisers are often inert hydrocarbon compounds used to increase flexibility and processability of polymers by reducing their glass transition temperature. The International Union of Pure and Applied Chemistry (IUPAC) had defined plasticiser as a "substance or material incorporated in a material to increase its flexibility, workability, or distensibility" (Vierra et al., 2011). Plasticisers are expected to reduce the modulus, tensile strength, hardness, density, melt viscosity and glass transition temperature; meanwhile increasing the flexibility, elongation at break and toughness of polymer (Matthews, 1996).

Plasticisers can be either internal or external, where internal plasticisers are inherently part of the plastic and remain part of the product while external plasticisers are not bonded to polymer chains and can therefore be lost by evaporation, migration or extraction (Frados, 1976). External plasticisers can be further divided into two main groups that are the primary and secondary types. Primary plasticisers are more compatible with polymer enabling them to be used as the sole plasticizer or as the major component of plasticiser in polymer. On the other hand, secondary plasticisers are less compatible and will exude from polymer if used alone. Therefore, they are normally blended with primary plasticisers to improve certain performance properties and reduce cost (Wojciechowska, 2011). PVC medical device should fulfil criteria including low toxicity, low migration, transparency, flexibility, strength, elasticity, stability at low and high temperatures, chemically inert as well as permeability to water, oxygen and carbon dioxide in the desired range. Thus, a good plasticiser should have high boiling point, low volatility, light colour, resistance to chemical reaction, non-toxic and low cost. Several plasticisers may be mixed to achieve the desired properties of the end product as no single plasticiser is capable to satisfy all the criteria.

2.1.1 Mechanisms of Plasticisation

Plasticisers are able to increase flexibility of polymers, but how do they work? Several theories were developed to explain the concept of plasticisation (Krauskopf & Godwin, 2005).

The Lubricating Theory states that upon heating, plasticiser molecules will diffuse into the polymer matrix weakening the polymer-polymer interaction (Van der Waals forces). These molecules act as shields to prevent formation of rigid networks when the polymer is cooled to ambient temperature again. This mechanism reduces the PVC glass transition temperature and allows the polymer chains to move rapidly, increasing the flexibility, softness and elongation (Krauskopf & Godwin, 2005).

The Gel Theory assumes that polymers and plasticisers molecules are loosely held together by an internal, three-dimensional network of weak secondary bonding forces. These bonding forces are easily overcome when external stress is applied, allowing the plasticised polymer to bend, elongate and compress. The presence of plasticiser molecules have separated the polymer chains, increased the space between polymer molecules and in turn reduced the rigidity of the gel structure. Besides that, plasticiser molecules that are not attached to polymer chains are tend to aggregate, allowing the polymer molecules to move more freely, thus enhancing the gel flexibility (Krauskopf & Godwin, 2005).

Free Volume Theory states that the presence of a plasticiser lowers the glass transition temperature of polymer. Free volume is a measure of internal space available within a polymer matrix. In glassy state, the molecules are packed closely and the free volume is low. The molecules cannot move past each other easily creating rigid and hard polymer. When the polymer is heated to above the glass transition temperature, molecules absorb the thermal energy and vibrate more vigorously creating additional free volume which allows the molecules to move past each other rapidly. This makes the polymer system more flexible and rubbery. When the plasticiser molecules are added to separate the PVC molecules creating more free volume, the glass transition temperature is reduced, increasing the flexibility of polymer (Krauskopf & Godwin, 2005).

The Mechanistic Theory considers that plasticiser molecules are not bound permanently to the polymer chains, but are free to associate and dissociate with the amorphous sites of polymer molecules. Since the interactions between plasticiser and polymer molecules are weak, there is a dynamic exchange process where one plasticiser molecule attached at a site is readily dislocated and replaced by another. Different plasticisers possessed different strength in plasticiser-polymer and plasticiser-plasticiser interactions. At low plasticizer levels, the plasticiser-polymer interactions are dominant; while at high plasticizer concentrations, plasticiser-plasticiser interactions predominate. This has explained the occurrence of “antiplasticization” phenomenal, where low plasticizer levels increase rigidity in PVC (Krauskopf & Godwin, 2005).

2.1.2 Classification of Plasticisers

There are over 100 types of plasticisers available commercially which can be categorized into general purpose plasticisers, specialty plasticisers, organic plasticisers and others. Some commonly used plasticisers are discussed as follow.

2.1.2.1 Phthalates

Phthalates, commonly refer to esters of orthophthalic acid, are the most widely used and discussed plasticisers in the world. They can be produced by reacting two moles of monohydride alcohol with one mole of phthalic anhydride. The alcohol used are normally range from C_4 to C_{13} as phthalates produced from alcohols below C_4 are too volatile while from alcohols above C_{13} have limited compatibility (Krauskopf & Godwin, 2005). The general structural formula of phthalates is shown in Figure 2.1 where the functional groups, R, can either be linear aryl groups or alkyl groups with aromatic ring.

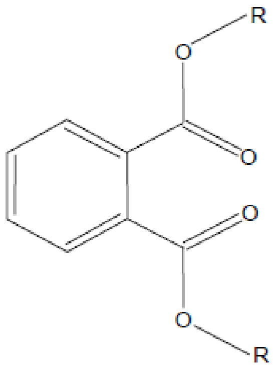


Figure 2.1: General Structural Formula of Phthalates (Source: Maag et al., 2010)

In general, phthalates possess most desirable properties of plasticisers including good compatibility, high gelling capacity, relatively low volatility at ambient temperature, water resistant and low cost (Rahman & Brazel, 2004). As the length of functional group increases, the plasticising effect, gelling capacity and volatility decreases. This means that higher concentration of plasticiser is required to achieve same flexibility but the extractability will be reduced.

Some of the examples of phthalates plasticisers are di(2-ethylhexyl) phthalate (DEHP), di-n-butyl phthalate (DBP), diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP). Among all these, DEHP which was introduced in 1930 is the most widely used plasticisers in the world. DEHP having shorter chain offers higher compatibility and plasticising effect. However, leaching problems occurs especially in medical device have hindered its application. The trend is gradually changed to higher molecular weight phthalates such as DINP that has comparable price. Although DINP offers lower plasticising efficiency, the problem of plasticiser leaching can be greatly reduced (Krauskopf & Godwin, 2005).

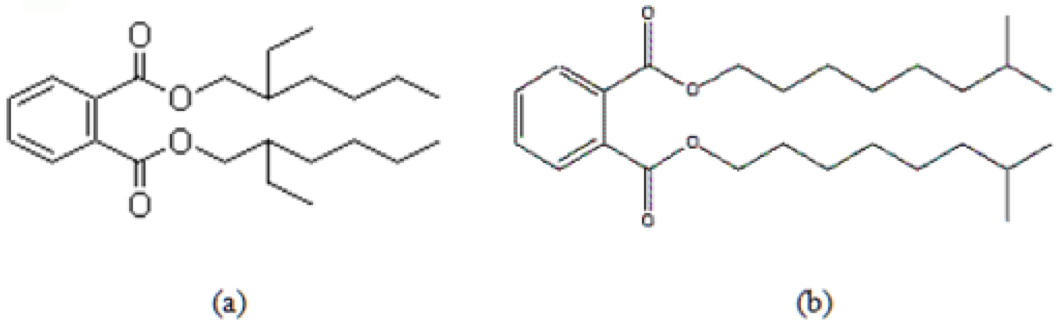
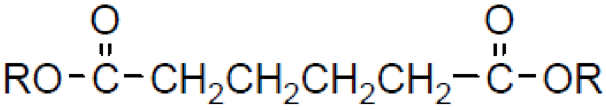


Figure 2.2: Structural Formula of (a) DEHP and (b) DINP
(Source: Gil et al., 2006)

2.1.2.2 Adipates

Adipates are esters of adipic acid which are produced by esterification reaction with monohydride alcohol range from C_8 to C_{10}. Generally, lower molecular weight alcohols are reacted with higher molecular weight acids or vice versa to produce adipates range between C_{18} and C_{26}. This is to maintain the apolar/polar ratio to provide sufficient PVC compatibility along with low temperature properties (Krauskopf & Godwin, 2005). Adipates with molecular weight of 300 – 350 tend to be too volatile while those with molecular weight more than 400 have limited compatibility with PVC (Krauskopf, 1988). The structural formula of adipates is shown in Figure 2.3 where R is alkyl group.



$$RO-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_2CH_2-\overset{\overset{O}{\|}}{C}-OR$$

Figure 2.3: General Structural Formula of Adipates (Source: Wypych, 2004a)

The reduction of glass transition temperature by adipates is lower compared to the corresponding phthalates, but they flexibilize the amorphous sites of PVC more efficiently. Thus, they impart higher flexibility with lower molecular weight and specific gravity (William, 2005). Besides that, adipates perform better in low temperature flexibility and are relatively safe compared to phthalates. However, they have higher volatility which causes high migration rate and are more costly than phthalates. As the molecular weight of adipates increases, the volatility decreases but at the same time the solubility and compatibility with PVC will also decrease. Fortunately, the influence of compatibility is very small and a substantial increase in volatility is capable to compensate the changes in compatibility. Thus, adipate plasticisers are more permanent when their molecular weight increases.

Examples of adipate plasticiser are di-2-ethylhexyl adipate (DEHA), dibutyl adipate (DBA), diisononyl adipate (DINA) and diisodecyl adipate (DIDA). DEHA as the most commonly used adipate plasticiser in PVC is a product of esterification of 2-ethylhexanol with adipic acid. (Krauskopf & Godwin, 2005). Other than that, for application requiring lower plasticiser volatility, DINA with higher molecular weight is a good alternative. Due to the high cost of adipates, they are commonly blended with other plasticisers such as phthalates to compromise low temperature properties and the cost.

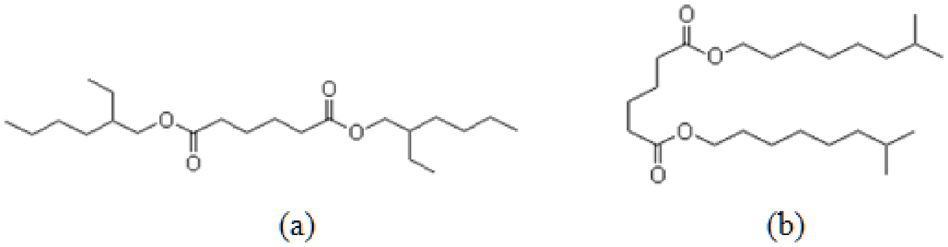

(a) (b)

Figure 2.4: Structural Formula of (a) DEHA, and (b) DINA
(Source: Gil et al., 2006)

2.1.2.3 Epoxides

Epoxides plasticisers are epoxidized natural products having oxirane oxygen groups in their molecules that are formed by the epoxidation of olefinic double bond in their raw material. They normally come from soybean oil or linseed oil with unsaturated fatty acids such as oleic, linoleic and linolenic that can be epoxidised with hydrogen peroxide or peracetic acid.

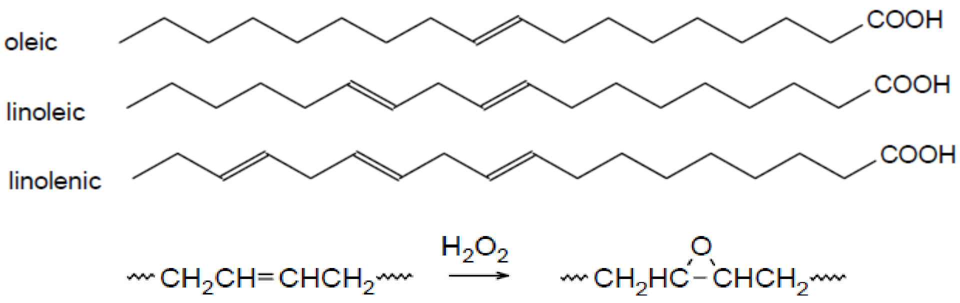


Figure 2.5: Unsaturated fatty acid of soybean oil and the epoxidation reaction
(Source: Wypych, 2004b)

Two examples of most widely used epoxides plasticisers are epoxidised soybean oil (ESO) and epoxidised linseed oil (ELO). They are used as secondary plasticiser and secondary stabiliser in PVC due to their ability to form bonds with the hydrogen chloride when PVC is decomposed. Epoxides plasticisers are the only class of plasticisers that undergo side chain bonding onto PVC chain at the site of labile chlorides in the presence of stabilizers (Krauskopf & Godwin, 2005). They have very high molecular weight (approximately 1000), hence they have low volatility and can hardly migrate out. ESO was previously tested as primary plasticizer with high concentration (approximately 50 phr), but the result is not satisfactory as photo-oxidation or hydrolysis of the oxirane oxygen occurs after long time UV-exposure, resulting in sticky surfaces (Lutz, 1993). Thus, ESO is normally work as secondary plasticisers and blended with other plasticisers such as phthalates during application.

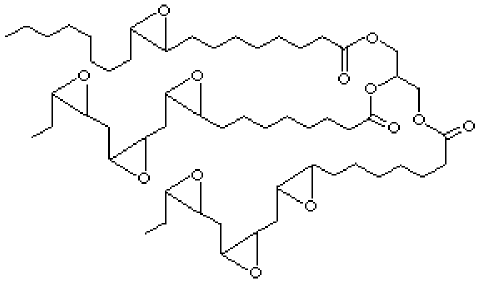


Figure 2.6: Structural Formula of Epoxidised Soybean Oil
(Source: Maag et al., 2010)

2.1.2.4 Terephthalates

Terephthalates refer to para-phthalates that are one of the isomeric structures of phthalates. They are esters of terephthalic acid which are produced by reacting terephthalic acid with monohydride alcohol similar to phthalates. The most common terephthalates is di(2-etylhexyl) terephthalates (DEHTP) or sometime refers as dioctyl terephthalate (DOTP). The manufacturing cost and plasticising efficiency is similar to DEHP but with better low temperature properties and significant lower volatility due to high molecular weight and long hydrocarbon chain. Thus, DOTP can be considered as a good alternative to replace volatile and toxic DEHP.

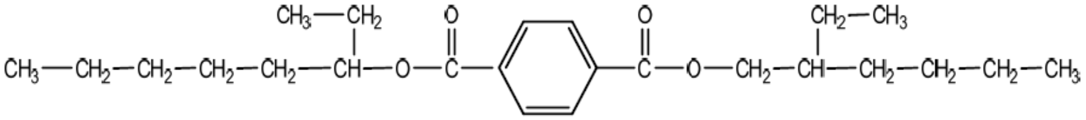


Figure 2.7: Structural Formula of Dioctyl Terephthalate (DOTP).
(Source: Nexant Inc., 2008)

2.1.2.5 Trimellitates

Trimellitates are the products of esterification between three moles of monohydride alcohols and one mole of trimellitic anhydride (TMA) which has similar structure with phthalic anhydride except for the third carbonyl group on the aromatic ring. This additional carbonyl group has contributed to higher molecular weight compared to phthalates and the third ester group contributes sufficient polarity to maintain PVC compatibility (Krauskopf & Godwin, 2005).

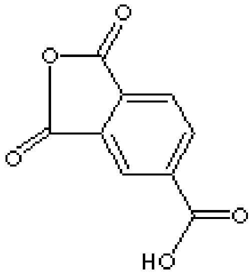


Figure 2.8: Structural Formula of Trimellitic Anhydride (TMA)
(Source: Wypych, 2004a)

Due to high molecular weight and highly branched isomeric structures, trimellitates plasticiser possessed very low diffusivity and high temperature stability. The oxygen and carbon dioxide permeability is also enhanced as plasticiser concentration increases. These features have encouraged their application in medical device especially for blood and intravenous solution container and tubing where leaching and permeability are the major concern. However, the oil extraction resistance is similar to phthalates. The plasticising efficiency is also relatively low and the cost is higher as compared to phthalate. Thus, higher concentration is needed to attain the required flexibility consequently induce higher manufacturing cost. Besides that, at high plasticiser level, PVC will become very soft and sticky especially after sterilization by autoclaving (Terumo Penpol Limited, 2011). In view of the high manufacturing cost and relatively low efficiency, trimellitates plasticiser is not suitable for application in disposable medical devices such as urine bag and tubing.

Common trimellitate plasticisers are trimethyl trimellitate (TMTM), tri-2-ethylhexyl trimellitate (TEHTM, also called trioctyl trimelliate (TOTM)) and octyl dibenzyl trimellitate. TOTM is the most widely used trimellitate plasticiser due to its extremely low diffusivity and low toxicity. If the price can be reduced by mass production, it is a good consideration for medical application.

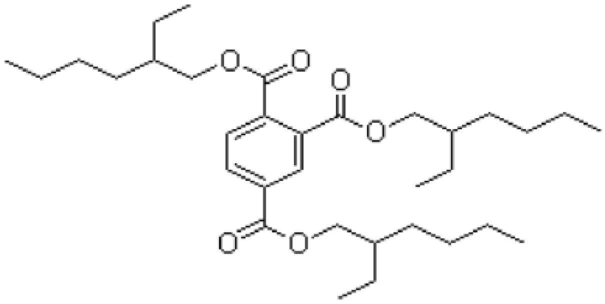


Figure 2.9: Structural Formula of Tri-2-etylhexyl Trimellitate (TEHTM).
(Source: Maag et al., 2010)

2.1.2.6 Citrates

Citrates are bio-derived tetraesters that are produced by reacting one mole of citric acid with three moles of alcohols. Citrate plasticiser being commercialized for more than 35 years, is one of the major contenders to replace toxic phthalate plasticiser typically DEHP due to its high miscibility, high efficiency and low toxocity. Toxicity tests conducted by the Pfizer Drug Safety Evaluation Department have proved that citrates are safe through acute dermal toxicity and ocular irritation tests in rabbits, and acute oral toxicity tests in mice and rabbits (Edenbaum, 1992). It is approved for use in sensitive application such as pharmaceutical tablet coatings, medical devices including blood bag, toys, food wraps and cosmetic products. Apart from that, a test conducted by Morflex Inc. showed that Citroflex B-6 (n-butyryltri-n-hexyl citrate) combined with ESO give similar properties to PVC as DEHP does (Edenbaum, 1992). However, it is easily extracted by lipid medium and the cost is much higher than DEHP.

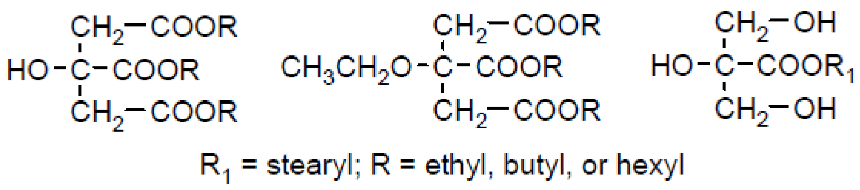


Figure 2.10: Chemical Structures of Citrates Used in Commercial Plasticisers (Source: Wypych, 2004a)

Examples of citrate plasticiser used in PVC are trimethyl citrate (TMC), tributyl citrate (TBC), acetyl tributyl citrate (ATBC), acetyl trihexyl citrate (ATHC), and butyryl trihexyl citrate (BTHC). In 2004, the European Union Scientific Toxic Committee stated that ATBC did not possess safety concern when young children placed PVC toys in their mouths and had approved its use in soft PVC toys (Nexant Inc., 2008). Besides that, ATBC offers high heat stability and does not discolour when processed in compounded resins.

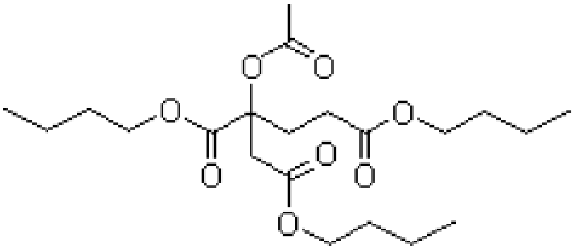


Figure 2.11: Structural Formula of Acetyl Tributyl Citrate (ATBC) (Source: Wypych, 2004a)

2.1.2.7 Di-isononyl-cyclohexane-1,2-dicarboxylate (DINCH)

Di-isononyl-cyclohexane-1,2-dicarboxylate (DINCH) is an ester produced by hydrogenation of the aromatic ring in DINP in the presence of noble catalyst as shown in Figure 2.12. It was introduced in 2002 by the company BASF and marketed under the Hexamoll name for sensitive applications such as medical devices, toys and food packaging where exposure to toxicological material is of great concern. According to BASF, Hexamoll® DINCH is a colourless, clear and practically anhydrous liquid with hardly noticeable odour and is compatible with almost all of the monomeric plasticisers commonly used in PVC.

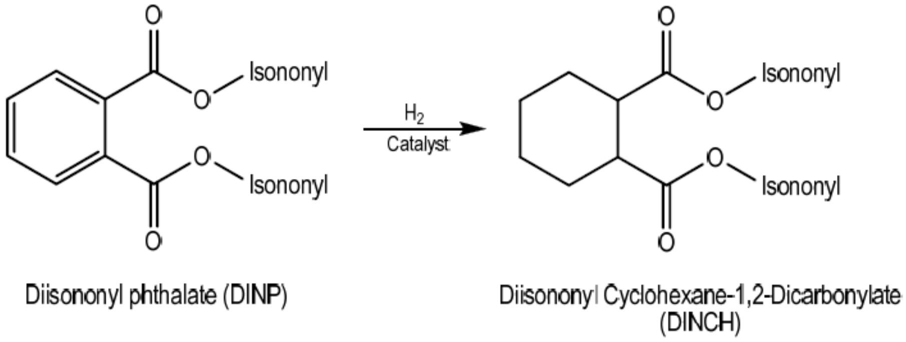


Figure 2.12: Production of DINCH by Hydrogenation of DINP
(Source: Nexant Inc., 2008)

Since it is the hydrogenated product of DINP, the performance characteristic of DINCH in PVC is expected to be similar to DINP but with lower compatibility due to increasing apolarity. With this, more plasticiser is needed to achieve the same flexibility. However, high loading of DINCH will cause the PVC to become very soft and sticky typically after autoclaving (Terumo Penpol Limited, 2011). To overcome this problem, PVC resins with higher K value should be used.

2.1.3 Leaching of Plasticisers and its Prevention

During compounding, plasticisers are not bonded to the polymer but just embedded into the polymer matrix. Thus, plasticiser molecules tend to diffuse out from the polymer matrix due to extraction by solvents, surface rubbing, volatility, migration, or degradation mechanisms. Plasticized polymers used to manufacture medical devices are often in contact with stationary or flowing fluids which are highly susceptible to plasticiser leaching. This leaching problem has become a critical issue in the world due to the toxicity of plasticisers and the shortening of material useful life.

Among various types of plasticisers, phthalate plasticiser particularly DEHP has become a target of worldwide scrutiny due to its potential carcinogenicity and possible endocrine modulating effects (Tickner et al., 2001). The leaching of DEHP may depend on the temperature, amount of plasticiser present, agitation of the device, medical solutions storage time and the type of medium being stored in or moving through the medical device. Many studies on the leachability of DEHP from PVC have been done. One of it by Kambia et al. (2001) stated that an average DEHP quantity of 123 mg was extracted from tubing during a 4 hour dialysis session, of which approximately 27 mg was retained in the patient’s body. Apart from toxicity, it is found that PVC has failed to retain its flexibility when the plasticisers leached out from the polymer.

Despite shifting towards low diffusivity and non toxic plasticisers, a few surface modification techniques were developed to reduce plasticiser leaching. The proposed methods are surface crosslinking, modification of surface hydrophilicity/ lipophilicity and surface coating (Rahman & Brazel, 2004). However, these techniques can only reduce the leaching tendency but not eliminate it.

2.1.3.1 Surface Crosslinking

Surface crosslinking is one of the most commonly studied techniques and often employed with other surface modification techniques to prevent leaching of plasticizers. The crosslinked polymer surface acts as a barrier to prevent transportation of plasticiser molecules between the polymer interface and external medium. Jayakrishnan and Lakshmi (1998) have tried to immobilize DEHP molecules by sulfonation process whereby the sulphur groups formed crosslinking on the PVC surface with presence of catalyst, creating a barrier within the PVC sufficient to retard the diffusion of DEHP molecules. It was shown that the resulting DEHP leaching was greatly reduced to a negligible level when tested over prolonged periods of time, using accelerated leaching conditions in the laboratory.

Audic et al. (2001) also investigated the effect of plasma induced surface crosslinking on flexible PVC packaging films in limiting leaching of plasticiser molecules into fatty foodstuff. It is found that Argon plasma gives the best result due to high degree of crosslinking during plasma treatment and further formation of oxygen based functional groups when the samples were re-exposed to air. The leaching tendency also reduced with increasing plasma treatment time.

2.1.3.2 Modification of Surface Hydrophilicity/Lipophilicity

Surface modification by grafting water soluble polymers to the surface of biomaterials has been studied by several researchers. For example, study by Krishnan et al. (1991) demonstrated that flexible PVC sheets grafted with N-vinyl pyrrolidone using ionizing radiation from ^{60}Co source showed significant reduction in plasticiser leaching into strong organic extractant (n-hexane). Incorporation of crosslinking agent such as ethylene dimethacrylate during grafting even further reduced the plasticizer leaching. Besides that, PVC treated with excess sodium polyethylene glycol (Na-PEG) has reduced leaching of DEHP into petroleum ether, cottonseed oil and paraffin oil considerably (Lakshmi & Jayakrishnan, 1998). It is assumed that the reduction is due to the hydrophilic PEG surface which acts as a barrier to the diffusion of DEHP from the PVC matrix.

Apart from that, flexible PVC can undergo nucleophilic substitution by sodium azide in aqueous media with tetrabutyl ammonium bromide as phase transfer catalyst (Jayakrishnan & Sunny, 1996). The azidated PVC surface was then irradiated by ultraviolet rays to crosslink the surface. It was found that the DEHP leached into hexane was reduced considerably depending on the extent of azidation of the PVC surface and the irradiation dose. However, obvious colour change was observed probably due to dehydrochlorination occurred during grafting process and the elongation at break was reduced by 35 % resulting from the surface crosslinking.

2.1.3.3 Surface Coating

Plasticised PVC can be coated with some non-migrating material on the surface to reduce plasticiser migration. Breme et al. (2000) had developed a new plasma-assisted chemical vapour deposition (PACVD) process to coat polymer with titanium-based layer at very low temperature. The coating was found to be effective in preventing leaching of DEHP from PVC and potentially improve the blood compatibility of polymers. Apart from that, several researchers such as Karle et al. (1997) had studied the effect of heparin coating on DEHP leaching and concluded that it is capable to reduce the extraction of DEHP as well as the metabolites, monoethylhexyl phthalate (MEHP) but cannot completely prevent it.

2.2 Effectiveness of Plasticisers

The efficiency of plasticisers is defined as the amount of plasticizer required to achieve desired mechanical properties for interested material (Sothornvit & Krochta, 2005). The key performance properties such as the compatibility and miscibility with polymer, plasticising efficiency, low temperature properties, diffusivity, volatility and stability to degradation are largely dependent on the chemical structure of plasticisers, the molecular weight and functional groups and the concentration of plasticisers (Krauskopf & Godwin, 2005).

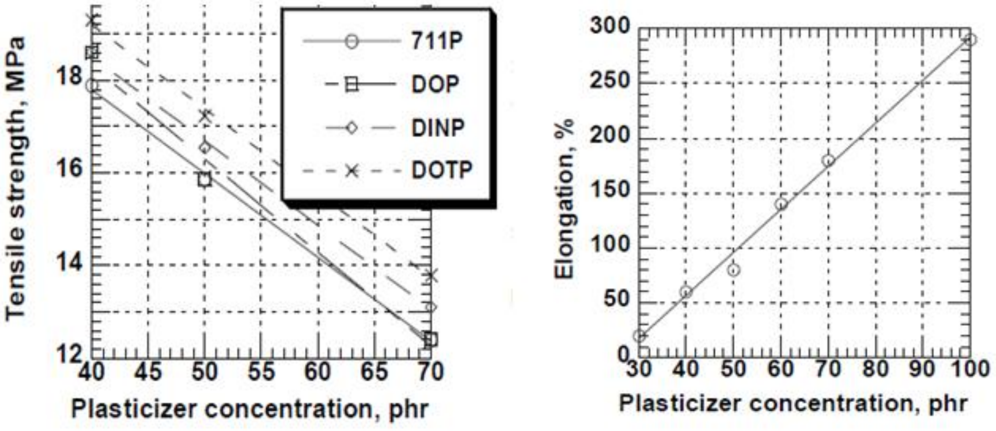
The compatibility and miscibility of plasticisers are dependent on the polar/apolar ratio of functional groups. Functional groups such as carbonyl group and aromatic rings impart higher miscibility while long, plain hydrocarbon chain adds apolarlity, reducing the compatibility. Generally, high compatibility is preferred, but plasticisers with too high compatibility will tend to dissolves the crystalline parts of the polymer and thereby breaks the polymer apart. On the other hand, plasticisers with linear hydrocarbon chains impart higher flexibility in polymer as large branching tends to retard the movement of polymer chain when external force is applied. Next, the volatility and diffusivity of plasticiser molecules are affected by the molecular weight and size of plasticisers. Plasticisers with lower molecular weight and smaller size are generally more volatile while those with higher molecular weight and larger size can retain longer in the polymer. Lastly, the low temperature performance is enhanced by plasticisers with linear hydrocarbon chain typically adipates that have lower inherent viscosity at low temperature. The performance is decreased with increasing branching in plasticisers.

2.3 Effect of Plasticisers on Mechanical and Physical Properties

2.3.1 Tensile Strength and Elongation at Break

Tensile strength and elongation at break is another common indication of plasticiser efficiency that can be tested in accordance to ASTM D 638. Tensile strength is defined as the resistance of a material to a force tending to tear it apart (Matthews, 1996). Material with high tensile strength is able to absorb greater force without deformation. In contrast, low tensile strength material deforms easily to external force and tends to elongate before rupture.

Since addition of plasticiser increases the flexibility of polymer, it is expected that plasticised material holds lower tensile strength and larger elongation. The tensile strength and elongation at break depend primarily on the concentration and types of plasticisers. As concentration increases, PVC becomes more flexible which reduces the tensile strength and increase the elongation. The effect of plasticiser concentration on tensile strength and elongation is shown in Figure 2.13.



(a) (b)

Figure 2.13: Effects of Plasticiser Concentration on (a) Tensile Strength and (b) Elongation (Source: Wypych, 2004b)

Apart from that, the molecular weight of alcohol used in plasticiser also affects the tensile strength. The influence of plasticiser can be normalized by part per hundred resin (PHR) ratio as shown in Equation 2.1.

$$PHR\ ratio = \frac{PHR_{exp}}{PHR_{min}} \tag{2.1}$$

where

$$PHR_{exp} = \frac{mass\ of\ plasticiser}{mass\ of\ PVC} \times 100 \tag{2.2}$$

$$PHR_{min} = \frac{molecular\ weight\ of\ plasticiser}{molecular\ weight\ of\ one\ helical\ unit\ of\ PVC} \times 100 \tag{2.3}$$

PHR ratio of one indicates that there is one plasticiser molecule available to separate two chains in each helical unit (means all polar groups in PVC are isolated by monolayer of plasticizer). On the other hand, if PHR ratio equals to three, there is a substantial amount of free plasticizer in the polymer system. Figure 2.14 shows that tensile strength decreases with increasing number of carbon atom and decreasing PHR ratio.

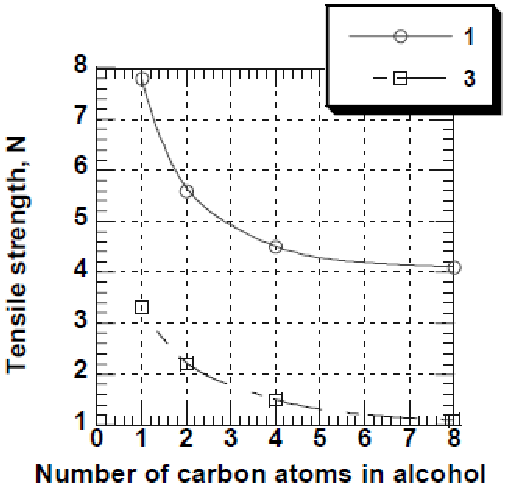


Figure 2.14: The Effect of Number of Carbon Atoms in Alcohol and PHR Ratio on Tensile Strength (Source: Wypych, 2004b)

2.3.2 Hardness

It is a common practice to quantify plasticisers' efficiency by PVC hardness which can be measured by Shore Hardness Test (ASTM D 2240) scale A for flexible polymer. Shore hardness can be defined as resistance of a material against the penetration by a cone. It is significantly influenced by the types and concentration of plasticisers. Generally, plasticisers with lower molecular weight give lower hardness value (softer). Besides that, hardness will decrease almost linearly with increasing plasticisers' concentration as shown in Figure 2.15.

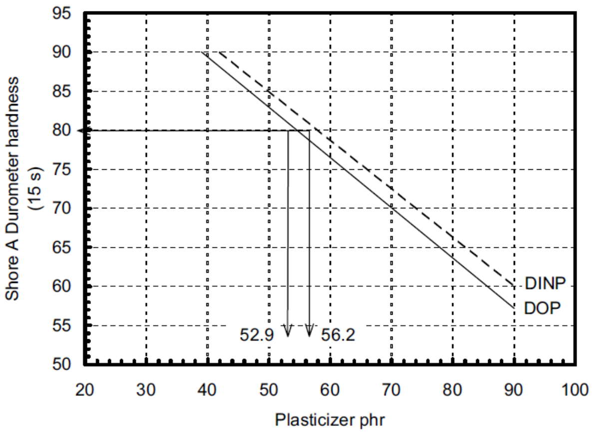


Figure 2.15: Hardness of PVC Plasticised with DINP and DOP at Different Amount (Source: Krauskopf & Godwin, 2005)

Apart from that, the hardness values can be used to calculate substitution factor (SF) which is the quantity of specific plasticiser needed to achieve Durometer A hardness of 80 relative to DEHP plasticiser as shown in Equation 2.4.

$$Substitution\,Factor\;(SF) = \left(\frac{phr\;plasticiser\;at\;Durometer\;\;80}{phr\;DEHP\;at\;Durometer\;\;80}\right) \qquad (2.4)$$

For example, the quantity of DEHP needed to achieve Durometer A Hardness of 80 was 52.9 phr while for DINP the quantity needed was 56.2 phr. Hence, the SF of DINP calculated from Equation 2.4 will be equal to 1.06.

$$Substitution\,Factor\;(SF) = \left(\frac{56.2\,phr\;DINP}{52.9\,phr\;DEHP}\right) = 1.06 \qquad (2.5)$$

This SF indicates that DINP is 6% less efficient than DEHP and needs to be added at a level of 6% higher than the DEHP to achieve the same hardness. It was found that this ratio is consistent over plasticiser level range from 20 to 90 phr (Leonard et al., 2005). The value of SF normally increases with increasing molecular weight of plasticiser. The SF for some common plasticisers is tabulated in Table 2.1.

Table 2.1: Molecular Weight and Substitution Factor for Some Common Plasticisers. (Source: Krauskopf & Godwin, 2005)

Plasticiser	Molecular Weight	Substitution Factor (SF)
DEHP	390	1.00
DINP	418	1.06
DIDP	446	1.10
DEHA	370	0.93
DINA	398	0.98
ESO	1000	1.10
DOTP	390	1.03
TOTM	546	1.17

2.4 Disposal of PVC Products by Incineration

Incineration is one of the most preferred disposal methods for various PVC wastes typically medical and construction wastes due to high degree of volume reduction, pathogens and hazardous organics elimination and the potential of energy recovery. However, emission of highly toxic pollutants such as polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofuran (PCDF) during inadequate or impropriate incineration has caused serious environmental problem. Both PCDD and PCDF are dioxins that are classified as carcinogenic substance by the World Health Organization (WHO) and also adversely affect the immune and endocrine system as well as development of foetuses (Suna et al., 2003). Besides that, dioxins are persistent in the environment as they tend to accumulate in the food chain and expose to all living things. It is recognized that incineration of organic substances in the presence of chlorine and metals is the major source of PCDD/ PCDF generation (Singh & Prakash, 2007). Thus, measures controlling and reducing emission of dioxins became the main interest for both industries and researchers.

The concentration of dioxins released from incinerator exhaust gas can be well controlled by employing high efficiency air pollution control devices including dry or wet scrubber, filter system and electrostatic precipitator. Both dry and wet scrubbers utilizing absorption method are efficient in removing dioxins and acid gases typically hydrogen chloride and sulphur dioxide. According to Linder et al. (1990), wet scrubbers can achieve 95 % emission control efficiency while bag house can only remove 30 % of dioxins based on eight municipal waste incinerators in California. Besides that, Fritsky et al. (2001) also developed a catalytic filter system that can destroy dioxins and turn them into non-toxic substance such as carbon dioxide. The remaining ashes containing toxic metals can be stabilized with cement to reduce the toxicity before disposal. Apart from that, electrostatic precipitator can also be used to separate particulate matters through different electrical charge while the collected particles can be removed by rapping or washing the surface of collecting medium.

According to Hahn et al. (1992), dioxins are usually formed under incomplete combustion or in the cooler zone of incinerator at temperature range from 240 – 450 ℃. Thus, by elevating the combustion temperature to more than 800 ℃, the generation of dioxins can be greatly suppressed. Examples of high temperature incinerators are starved air incinerator, excess air incinerator and rotary kiln. Hydrogen chloride produced during incineration is then recycled for vinyl chloride monomer (VCM) and PVC production as a way to close the chlorine loop. However, high temperature incineration is only applicable to large scale incinerators. Dioxins released from small scale incinerators and open burning in the field or backyard should also be controlled. One of the controlling methods is by incorporating calcium carbonate into the PVC wastes. Since calcium carbonate is common filler, PVC products that had sufficient amount of filler may be incinerated directly. A treatment process developed by NKT Research Centre can transform PVC with its additives into calcium chloride, a metal concentrate and energy rich coke and oil for other applications (Jaksland et al., 2000). In this process, recovery of more than 98 wt% lead and 99 wt% chlorine originated from PVC wastes was reported and plasticisers were degraded. No dioxins were detected and concentration of halogenated hydrocarbons in gas and liquid product was low. Another group of researchers also found that by adding calcium carbonate with small amount titanium dioxide (TiO_2), the dioxins concentration can be greatly suppressed in both exhaust gas and the resulting ashes. Suna et al. (2003) proved that the addition of calcium carbonate into PVC wastes trapped the dioxins in the ash and thus reducing the emission of dioxin through stack gas. The resulting ashes were then irradiated with UV light or sunlight where titanium dioxide photocatalyst will decompose the dioxins before disposal. The efficiency of photocatalyst may be affected by its dispersion in the polymer matrix. It is reported that low dispersity of titanium dioxide due to agglomeration had led to catalytic activity reduction during incineration. Kim et al. (2008) tried to attach the titanium dioxide to hyperbranch poly(ε-caprolactone) (HPLC) and found that the photocatalytic degradation of PVC with HPLC-TiO_2 under UV radiation were improved. The results showed that HPLC-TiO_2 with a maximum TiO_2 loading of 1.6 wt% can achieve up to 60 – 70 % of dioxins removal which is equivalent to 1.5 times of TiO_2 prepared from conventional method.

CHAPTER 3

METHODOLOGY

3.1 Materials

The base polymer of this study, suspension grade polyvinyl chloride (PVC) powder of K value 71, was supplied by Thai Plastic and Chemicals Public Company Limited. Commercial grade plasticisers including diisononyl phthalate (DINP), dioctyl terephthalate (DOTP), dioctyl adipate (DOA), and epoxidized soybean oil (ESO Cizer LX-118) used to plasticise PVC were supplied by Luxchem Trading Sdn Bhd, Malaysia. Liquid form thermal stabiliser, Calcium/Zinc Stearate (Ca/Zn GS-T66) used to stabilise PVC blends against heat was supplied by Golden Chemical Corp., Malaysia. The external lubricant, ethylene bis-stearamide (Akrowax® EBS 290) used to lubricate PVC blends during sample preparation was supplied by Akrochem Corporation, Malaysia.

3.2 Equipments

Equipments required to carry out experiments in this study were Accuweigh HP4200 Laboratory Scale, ChangDa SHR-10A high speed mixer, Frank two roll mill, Cabe Milano compression, Omnipotent Instruments hardness tester, Shimadzu Universal Testing Machine, MZ – 4102 sheet punching machine, dumbbell-shaped cutter, Matsuttaku Electronic Densimeter MH – 300E and Hitachi S-3400N scanning electron microscope.

3.3 PVC Compound Formulations

Three PVC compound formulations employing different types of plasticisers were used in this study. For each formulation, plasticiser loading level was varied while concentration of other chemicals such as PVC resin, secondary plasticiser ESO, Ca/Zn stabilizer and EBS lubricant were fixed. According to British Pharmacopeia 2010, the concentration of phthalate based plasticiser should be less than 40 wt%. Thus in formulation 2 (Table 3.2), both DINP and DOA were used to limit the weight percent of phthalate in each formulation. The concentration of chemicals was tabulated in Table 3.1 to 3.3.

Table 3.1: PVC Compound Formulation 1 (DOA/ESO)

Chemicals	**Concentration (phr)**				
	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**
PVC resin	100	100	100	100	100
DOA	40	50	60	70	80
ESO	3	3	3	3	3
Ca/Zn	2	2	2	2	2
EBS	0.3	0.3	0.3	0.3	0.3
Total (phr)	145.3	155.3	165.3	175.3	185.3

Table 3.2: PVC Compound Formulation 2 (DINP/DOA/ESO)

Chemicals	**Concentration (phr)**				
	Sample 1	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**
PVC resin	100	100	100	100	100
DINP	25	35	45	55	65
DOA	15	15	15	15	15
ESO	3	3	3	3	3
Ca/Zn	2	2	2	2	2
EBS	0.3	0.3	0.3	0.3	0.3
Total (phr)	145.3	155.3	165.3	175.3	185.3
% of DINP	17.2	22.5	27.2	31.4	35.1

Table 3.3: PVC Compound Formulation 3 (DOTP/ESO)

Chemicals	Concentration (phr)				
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
PVC resin	100	100	100	100	100
DOTP	40	50	60	70	80
ESO	3	3	3	3	3
Ca/Zn	2	2	2	2	2
EBS	0.3	0.3	0.3	0.3	0.3
Total (phr)	145.3	155.3	165.3	175.3	185.3

3.4 Sample Preparation

The formulations of PVC compound summarized in Tables 3.1 to 3.3 were first weighted. After that, PVC resin, Ca/Zn stabiliser, secondary plasticiser ESO and EBS lubricant were dry blended using high speed mixer operated at 1500 rpm to 85 °C. Corresponding plasticisers were then added into the PVC blend and mixed again till 110 °C. Next, the blended powders were preheated to 140 °C for 1 minute and two-roll milled at 140 °C for another 3 minutes to produce flat sheet with approximately 1 mm thickness.

Flat sheets from two roll mill were cut into square pieces with a dimension of 12 cm × 22 cm. To prepare sample for tensile test, 3 – 4 pieces of the cut flat sheets were placed on the mould of compression moulding machine to obtain specimen thickness of 3.2 ± 0.4 mm. On the other hand, to prepare sample for hardness test, 6 – 7 pieces of the cut flat sheets were placed on the mould of compression moulding machine to obtain specimen thickness of approximately 6 mm. The flat sheets in the mould were then heated to 170 °C for 5 minutes under pressure of 50 bar and subsequently compressed at same temperature and pressure of 100 bar for another 5 minutes. After that, the specimen was cooled and allowed to cure for 1 day before cutting into desired shapes.

3.5 Characterization Testing

3.5.1 Tensile Test

The dumbbell shape specimen was prepared in accordance to ASTM D 638 – 03 Type IV where the shapes and dimensions are shown in Figure 3.1 and Table 3.4 respectively. The dumbbell shape cutter was sized according to the specified standards to cut the specimen into desired dimensions.

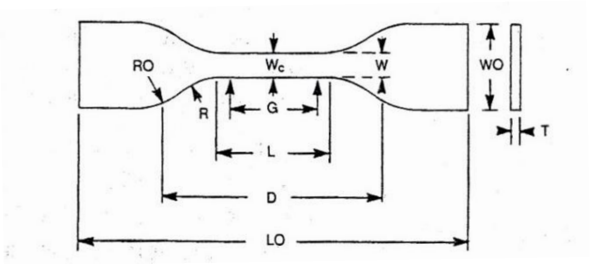


Figure 3.1: Dumbbell Shape Test Specimen Type IV (Source: ASTM D 638 – 03)

Table 3.4: Specimen Dimensions (Source: ASTM D 638 – 03)

Dimensions	**Length (mm)**
Width of narrow section (W)	6 ±0.5
Length of narrow section (L)	33 ±0.5
Width overall (WO)	19 + 6.4
Length overall (LO)	≥ 115
Gage length (G)	25 ±0.13
Distance between grips (D)	65 ±5
Radius of fillet (R)	14 ±1
Outer radius (RO)	25 ±1

The tensile test was conducted in accordance to ASTM D 638 – 03 with tensile tester at crosshead speed of 50 mm/min and a load of 1 kN. The tensile tester was calibrated before performing the tensile test. Meanwhile, thickness and width of specimens were measured and recorded. The dumbbell shape specimen was placed in the grips of the testing machine where the long axis of the specimen and the grips were aligned with an imaginary line joining the points of attachment of the grips to the machine. The specimen was aligned as perfectly as possible with the direction of pull to prevent slippage at the grips. The grips were then tightened evenly and firmly and the load was balanced. When the test started, the upper grip pull the specimen upward until it breaks and the tensile strength and percent elongation at break was measured. Ten specimens were replicated for each PVC compound formulation and the average as well as standard deviation of tensile strength and percent elongation at break was determined.

3.5.2 Hardness Test

The hardness test for flexible PVC was conducted in accordance to ASTM D 2240 – 05. In this study, Durometer Type A was selected and Type A indenter as shown in Figure 3.2 was used. The Durometer presser foot must be parallel to the specimen support table while the vertical distance between the presser foot and surface of test specimen was adjusted to 25.4 ± 2.5 mm. After that, specimen with a dimension of 30 mm × 30 mm was placed on the specimen support table in a way that the specimen area has a radius of at least 6 mm from the indenter point. When the specimen was properly positioned, the lever of operating stand was pressed to allow the indenter to be applied on the specimen. The reading of Durometer was then recorded after 15 s. The experiment was repeated 5 times for each PVC compound formulation and the arithmetic mean and standard deviation was calculated.

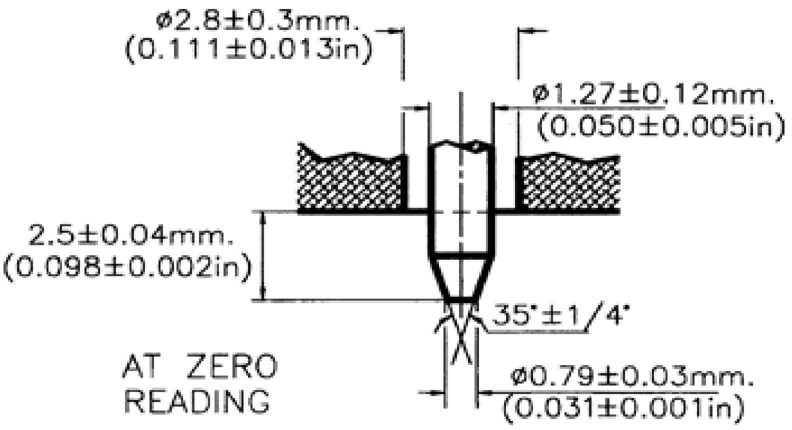


Figure 3.2: Type A Indenter (Source: ASTM D 2240 – 05)

3.5.3 Specific Gravity Test

The specific gravity for non-rigid vinyl chloride can be tested with Method A of ASTM D 792 – 00. The flat sheet from two roll mills was cut into square shape with dimension of 20mm × 20 mm × 1mm with smooth surface and edges. The specimen was then weighted in air and the mass was recorded. After that, specimen was immersed completely into the water at a temperature of 23 ± 2 ℃. Bubbles adhering to the specimen were removed by rubbing them with a wire. The mass of specimen in water was recorded again and the specific gravity of specimen calculated by the electronic densimeter was then determined and recorded. The procedures were repeated 3 times for each PVC compound formulation and the arithmetic mean and standard deviation was calculated. Meanwhile, the theoretical specific gravity for each formulation was calculated by equation 3.1.

$$specific\ gravity = \sum (wt\%)_i SG_i \tag{3.1}$$

where

$(wt\%)_i$ = weight percent of chemical i in the formulation

SG_i = specific gravity of chemical i

3.5.4 Scanning Electron Microscopy (SEM)

The fractured surfaces of specimens from tensile test were cut into small pieces with a thickness of approximately 3 mm at the point of rupture. The cut samples were then placed on the specimen stub by double-sided sticky tape and coated with a layer of gold and palladium to facilitate SEM examination. After the coating process, the samples were mounted on a stub and accommodated in the specimen chamber to observe the morphology of fractured surface. SEM photographs were taken at different sites and magnifications of 1000 and 5000 times.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Tensile Strength

Table 4.1 and Figure 4.1 show that the tensile strength of polyvinyl chloride (PVC) compounds decreased with increasing plasticiser concentration for all plasticiser types. This complied with the study by Wypych (2004b) where addition of plasticiser increased the flexibility of PVC and consequently reduced the tensile strength. As more plasticiser molecules diffused into the polymer matrix, the polymer chains became further apart and able to move when external force applied (Krauskopf & Godwin, 2005). Thus, as the specimens were pulled apart, the resistance to the pulling force was obviously reduced and tend to deform before ruptured. Figure 4.1 shows that the reduction of tensile strength was almost linear with plasticiser concentration for diisononyl phthalate, dioctyl adipate and epoxidised soybean oil added PVC compounds (DINP/DOA/ESO-PVC) and dioctyl terephthalate and ESO added PVC compounds (DOTP/ESO-PVC) but not for DOA and ESO added PVC compounds (DOA/ESO-PVC). The gradient for DOA/ESO-PVC was relatively high when plasticiser concentration was less than 60 phr but it dropped dramatically when it exceeded 60 phr. This shows that effect of plasticiser concentration on tensile strength of PVC compounds had become insignificant at high loading level of plasticiser.

Apart from that, Figure 4.1 and Table 4.1 also illustrate that DOA/ESO-PVC posed lowest tensile strength; followed by DINP/DOA/ESO-PVC and lastly DOTP/ESO-PVC. This shows that DOA could provide highest plasticising efficiency compared to DINP and DOTP. It is reasonable as linear chain plasticiser will not block the movement of polymer chains during stretching and thus impart higher flexibility (Rahman & Brazel, 2004). By referring to the molecule structure, DINP (Figure 2.2 (b)) should have more branching than DOTP (Figure 2.7). However, Figure 4.1 shows that DINP/DOA/ESO-PVC posed lower tensile strength than DOTP/ESO-PVC. This might be due to the presence of DOA which has higher plasticising efficiency in formulation 2 (DINP/DOA/ESO). The efficiency might be complemented and consequently provides lower tensile strength.

Table 4.1: Tensile Strength of Plasticised PVC Compounds

Plasticiser (phr)	**Tensile strength (N/mm2)**		
	DOA/ESO	**DINP/DOA/ESO**	**DOTP/ESO**
40	18.8 ±0.63	19.5 ±0.48	22.0 ±0.50
50	14.9 ±0.17	17.7 ±0.42	19.4 ±0.30
60	11.1 ±0.33	15.3 ±0.36	16.2 ±0.53
70	10.0 ±0.48	12.3 ±0.35	13.7 ±0.20
80	9.4 ±0.35	11.2 ±0.35	11.9 ±0.34

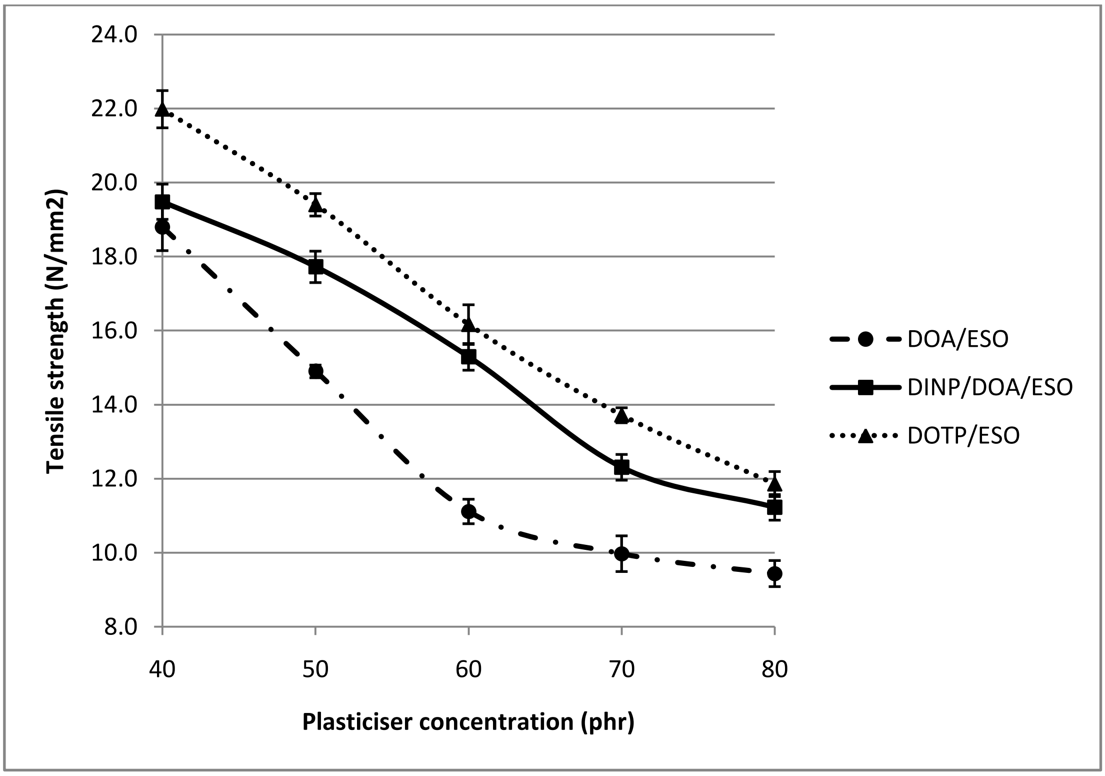


Figure 4.1: Tensile Strength of PVC Compounds Filled with Different Types of Plasticisers

4.2 Elongation at Break

Generally, elongation at break for PVC compounds increased with increasing plasticiser concentration as shown in Table 4.2 and Figure 4.2. The elongation at break of plasticised PVC samples was observed to be very high (ranging from 600 % to 1100 %) due to high loading level of plasticisers. As proposed by the Lubricating Theory, small plasticiser molecules diffused into the polymer matrix will weaken the attraction between polymer chains, enabling them to elongate upon stretching (Krauskopf & Godwin, 2005). At higher concentration, more plasticiser molecules separate the polymer chains apart and further weaken the secondary bonding force. As a consequent, less energy is needed to move the polymer chains and the samples could elongate further with same pulling force.

Apart from that, Figure 4.2 demonstrates that the elongation at break increased in a polynomial trend where the percentage of elongation increased rapidly at low plasticiser concentration but became less significant at high loading level of plasticiser. Since the plasticisers used in this study are external plasticiser, its miscibility with PVC is somehow limited especially at high plasticiser concentration. More voids might occur at high plasticiser loading as shown in Figure 4.3 and sections with voids are generally weaker and susceptible to failure when external load applied. Some points with exceptional high elongation at break such as DOA/ESO at 60 phr and DINP/DOA/ESO at 80 phr were observed. One of the possible explanations is that the plasticiser molecules were well distributed throughout the polymer matrix as shown in Figure 4.4. When external load applied to the polymer, the force was distributed evenly to the matrix and thus enhancing the mechanical property.

Among the plasticiser mixtures used in this study (DOA/ESO, DINP/DOA/ESO and DOTP/ESO), DOTP/ESO-PVC posed lowest elongation at break as shown in Figure 4.2. This indicates that DOTP/ESO holds lowest plasticising efficiency. On the other hand, the elongation at break of DOA/ESO-PVC was higher than DINP/DOA/ESO-PVC at low plasticiser concentration (< 60 phr) but found to be similar at loading level of 60 phr. As the plasticiser concentration exceeded 60 phr, the elongation at break of DOA/ESO-PVC was lower than

DINP/DOA. This might be due to the fact that DOA is less compatible with PVC resins typically at high plasticiser concentration. According to Krauskopf and Godwin (2005), plasticisers with functional group such as carbonyl group and aromatic rings are more compatible with PVC resin than those with long, plain hydrocarbon chain. Thus, DINP with benzene ring in the chemical structure is generally more compatible than linear chain DOA. The effect of compatibility might not be significant at low level of plasticiser loading but would become more obvious as the concentration of DOA increased.

Table 4.2: Elongation at Break of Plasticised PVC Compounds

Plasticiser (phr)	Elongation at break (%)		
	DOA/ESO	DINP/DOA/ESO	DOTP/ESO
40	777 ±23.3	693 ±22.4	663 ±25.2
50	940 ±18.6	867 ±23.2	786 ±16.4
60	918 ±34.7	919 ±32.1	855 ±28.3
70	922 ±53.6	939 ±34.1	884 ±18.9
80	951 ±45.5	1007 ±33.9	915 ±30.9

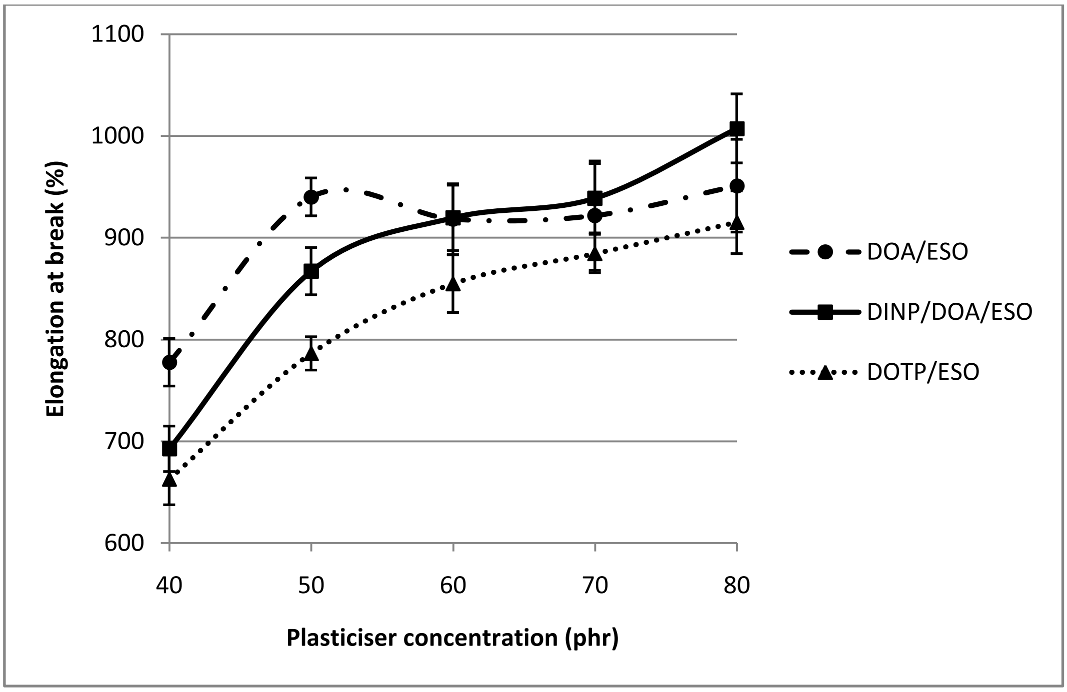
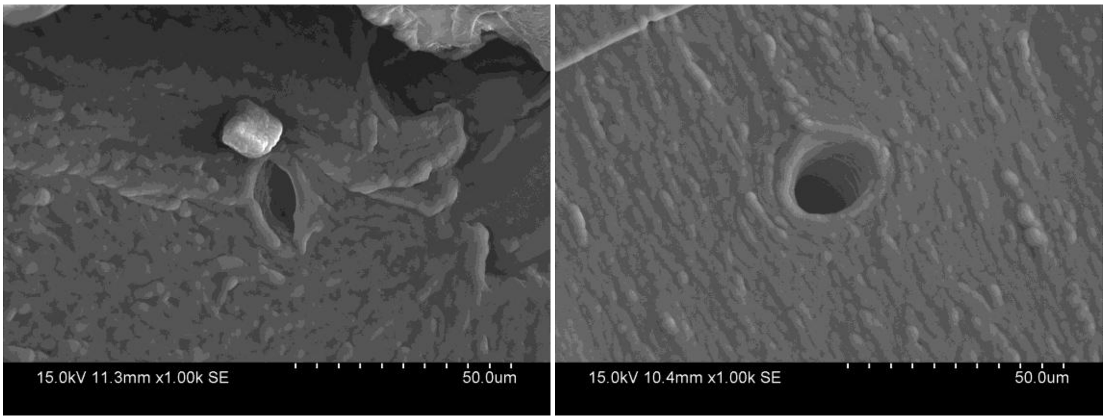
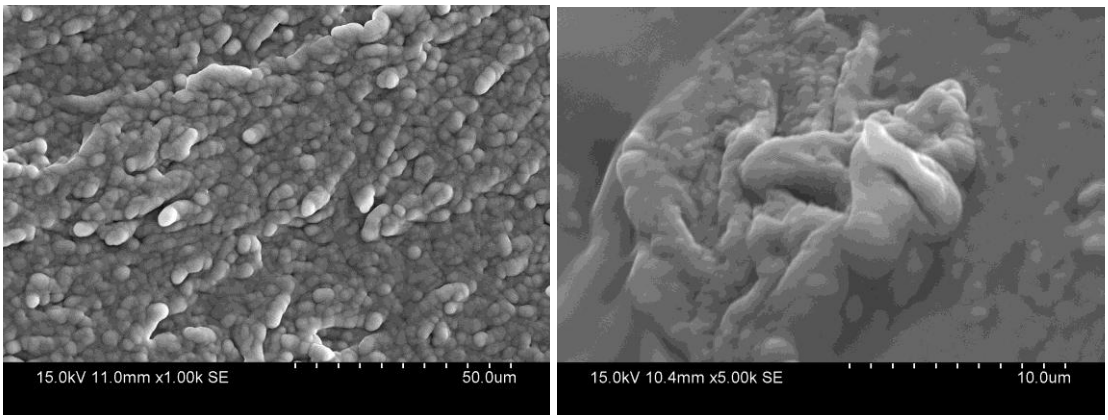


Figure 4.2: Elongation at Break of PVC Compounds Filled with Different Types of Plasticisers



(a) **(b)**

Figure 4.3: Void Appears in (a) Sample 4 and (b) Sample 5 of Formulation 1 (DOA/ESO) by Scanning Electron Microscopy (SEM)



(a) **(b)**

Figure 4.4: Morphologies of Fracture Surface for (a) Sample 3 of Formulation 1 (DOA/ESP) and (b) Sample 5 of Formulation 2 (DINP/DOA/ESO)

4.3 Durometer Hardness

The Durometer Hardness of PVC compounds decreased almost linearly with plasticiser concentration as shown in Table 4.3 and Figure 4.5. This is in line with the study of Wypych (2004b) which stated that addition of plasticiser would soften the PVC compound and consequently reduce the hardness. According to the Free Volume Theory, plasticiser molecules will separate the polymer chains and increase the free volume in the polymer matrix (Krauskopf & Godwin, 2005). Therefore, when the indenter pressed on the specimen’s surface, the free volume in polymer matrix allows the polymer chains to move further downwards, subsequently reducing the reaction force towards the indenter.

Based on Figure 4.5, DOA/ESO-PVC was observed to show lowest hardness value followed by DINP/DOA/ESO-PVC and lastly DOTP/ESO-PVC. This means that the efficiency of plasticiser mixtures in reducing PVC’s hardness follow a sequence of DOA, DINP/DOA and DOTP with DOA being the most efficient plasticiser. According to Krauskopf and Godwin (2005), plasticiser with lower molecular weight is more effective in reducing hardness of PVC compounds. The molecular weight of DOA, DINP and DOTP are 370, 418 and 390 respectively. As expected, DOA with lowest molecular weight was the most efficient. For the other two plasticisers, DOTP with lower molecular weight should have higher efficiency than DINP. However, Figure 4.5 shows that DINP/DOA/ESO-PVC posed lower hardness than DOTP/ESO-PVC. This is because DOA has complemented the efficiency of DINP in formulation 2 (DINP/DOA/ESO).

Table 4.3: Durometer Hardness of Plasticised PVC Compounds

Plasticiser (phr)	**Durometer Hardness**		
	DOA/ESO	**DINP/DOA/ESO**	**DOTP/ESO**
40	80.4 ±0.55	83.4 ±0.55	86.4 ±0.55
50	72.0 ±0.00	77.2 ±0.45	79.4 ±0.55
60	65.4 ±0.55	72.6 ±0.55	74.8 ±0.45
70	61.8 ±0.45	65.6 ±0.55	68.8 ±0.45
80	58.2 ±0.45	60.4 ±0.55	64.2 ±0.45

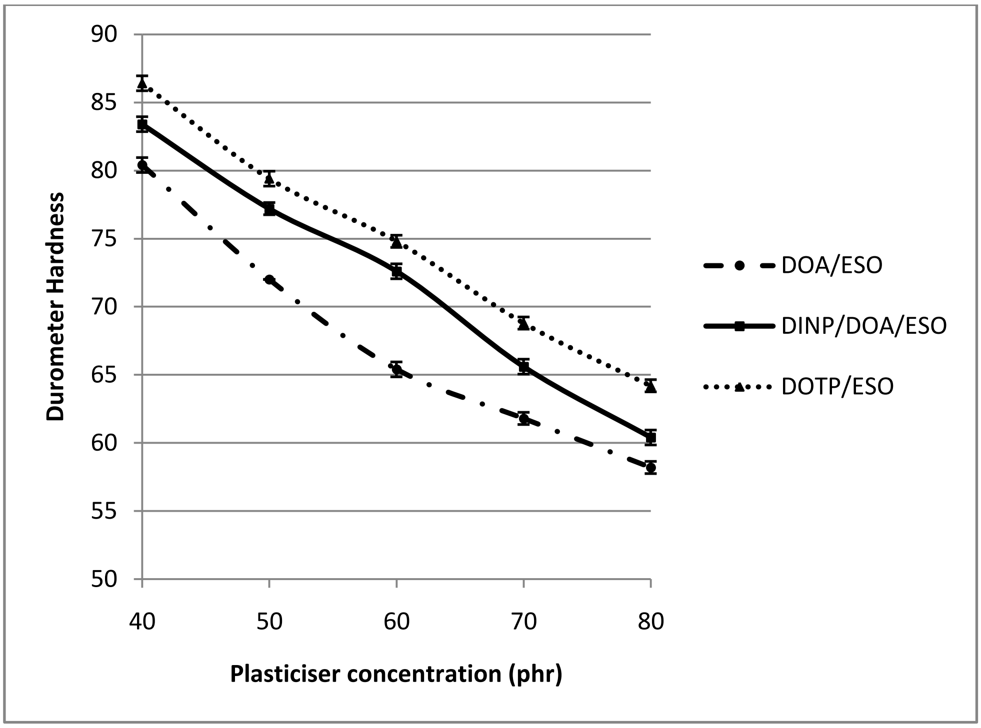


Figure 4.5: Durometer Hardness of PVC Compounds Filled with Different Types of Plasticisers

4.4 Specific Gravity

The theoretical specific gravity of PVC compounds was calculated by equation 3.1 as shown in section 3.5.3 using specific gravity of individual raw material tabulated in Table 4.4 as well as weight percent of chemicals in Tables 4.5 to 4.7. The calculated value was then compared with the experimental specific gravity obtained from the densimeter.

Table 4.4: Specific Gravity of Chemicals

Chemical	Specific Gravity
PVC	1.4
DOA	0.928
DINP	0.974
DOTP	0.985
ESO	0.99
Ca/Zn	0.969
EBS	0.97

Table 4.5: Weight Percent of Chemicals in Formulation 1 (DOA/ESO)

Chemical	Weight Percent				
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
PVC	0.688	0.644	0.605	0.570	0.540
DOA	0.275	0.322	0.363	0.399	0.432
ESO	0.021	0.019	0.018	0.017	0.016
Ca/Zn	0.014	0.013	0.012	0.011	0.011
EBS	0.002	0.002	0.002	0.002	0.002

Table 4.6: Weight Percent of Chemicals in Formulation 2 (DINP/DOA/ESO)

Chemical	Weight Percent				
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
PVC	0.688	0.644	0.605	0.570	0.540
DINP	0.172	0.225	0.272	0.314	0.351
DOA	0.103	0.097	0.091	0.086	0.081
ESO	0.021	0.019	0.018	0.017	0.016
Ca/Zn	0.014	0.013	0.012	0.011	0.011
EBS	0.002	0.002	0.002	0.002	0.002

Table 4.7: Weight Percent of Chemicals in Formulation 3 (DOTP/ESO)

Chemical	Weight Percent				
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
PVC	0.688	0.644	0.605	0.570	0.540
DOTP	0.275	0.322	0.363	0.399	0.432
ESO	0.021	0.019	0.018	0.017	0.016
Ca/Zn	0.014	0.013	0.012	0.011	0.011
EBS	0.002	0.002	0.002	0.002	0.002

Table 4.8 and Table 4.9 show the experimental and theoretical specific gravity of PVC compounds filled with different plasticiser mixtures respectively. The specific gravity of PVC compounds decreased with increasing plasticiser concentration for all plasticiser types as shown in Figures 4.6 to 4.8. This is because plasticisers have lower specific gravity than PVC resins. The specific gravity of a substance mainly depends on its density which considers the ratio of mass to volume.

Substance with low specific gravity normally has lower density and larger volume. As large volume substances such as plasticisers, stabiliser and lubricant embedded into the polymer matrix, the matrix was forced to expand, thus increasing the total volume. As a result, density of PVC compound was decreased and in turn reduced the specific gravity.

By comparing Figures 4.6, 4.7 and 4.8, the difference between theoretical specific gravity and the experimental specific gravity was largest for DOA/ESO-PVC (Figure 4.6) followed by DINP/DOA/ESO-PVC (Figure 4.7) and lastly DOTP/ESO-PVC (Figure 4.8). This shows that DOA was least compatible with PVC while DOTP was the most compatible among all plasticisers used in this study. As was mentioned before by Krauskopf and Godwin (2005), linear hydrocarbon chain plasticiser such as DOA is less compatible with PVC due to its non-polar nature. Whereas for DINP and DOTP, the presence of aromatic ring in their chemical structure has increased their polarity. These polar sides form stronger secondary bond with the polymer matrix, increasing the compatibility while reducing the total volume of PVC compound. The difference between experimental and theoretical specific gravity for DOTP/ESO-PVC was slightly smaller compared to DINP/DOA/ESO-PVC. One of the possible reasons is the presence of less compatible DOA in formulation 2 (DINP/DOA/ESO). Besides that, DOTP with symmetrical structure might pose better balance between polar and non-polar portion which could provide higher compatibility. The effect of compatibility was more significant at high plasticiser loading as shown in Figures 4.6 to 4.8 where the difference between experimental and theoretical specific gravity becomes larger as plasticiser concentration increased.

Table 4.8: Experimental Specific Gravity of Plasticised PVC Compounds

Plasticiser (phr)	**Experimental Specific Gravity**		
	DOA	**DINP/DOA**	**DOTP**
40	1.228 ± 0.0005	1.238 ± 0.0000	1.257 ± 0.0055
50	1.192 ± 0.0010	1.219 ± 0.0015	1.235 ± 0.0006
60	1.171 ± 0.0020	1.201 ± 0.0015	1.209 ± 0.0065
70	1.160 ± 0.0021	1.187 ± 0.0029	1.196 ± 0.0030
80	1.147 ± 0.0015	1.163 ± 0.0041	1.183 ± 0.0012

Table 4.9: Theoretical Specific Gravity of Plasticised PVC Compounds

Plasticiser (phr)	**Theoretical Specific Gravity**		
	DOA	**DINP/DOA**	**DOTP**
40	1.255	1.263	1.270
50	1.234	1.244	1.252
60	1.215	1.228	1.236
70	1.199	1.213	1.222
80	1.184	1.200	1.209

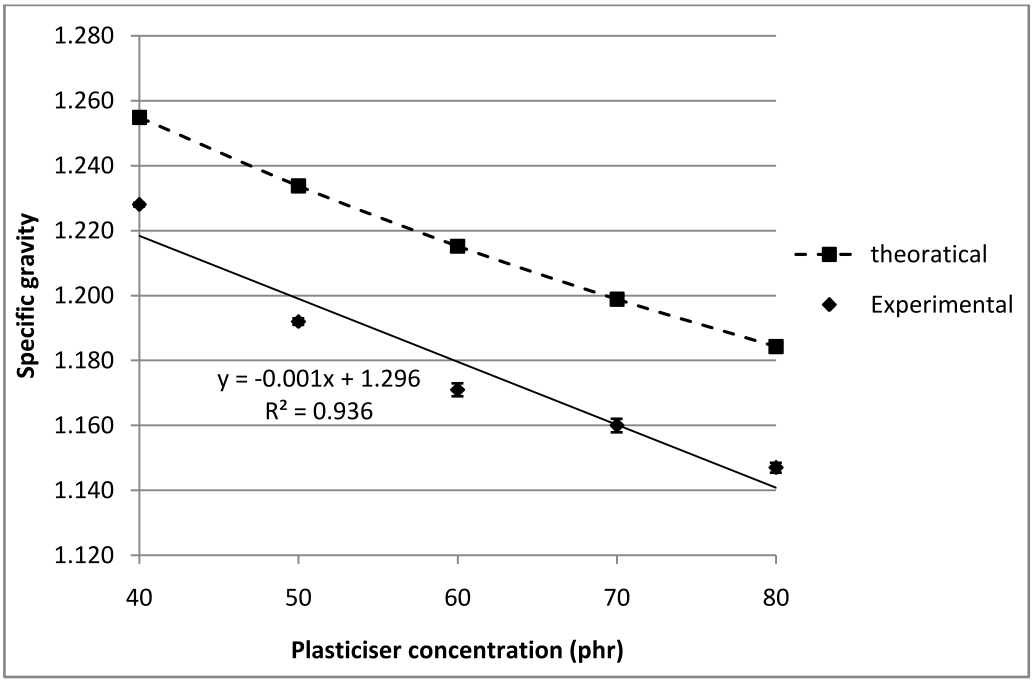


Figure 4.6: Specific Gravity of PVC Compounds Plasticised with DOA/ESO

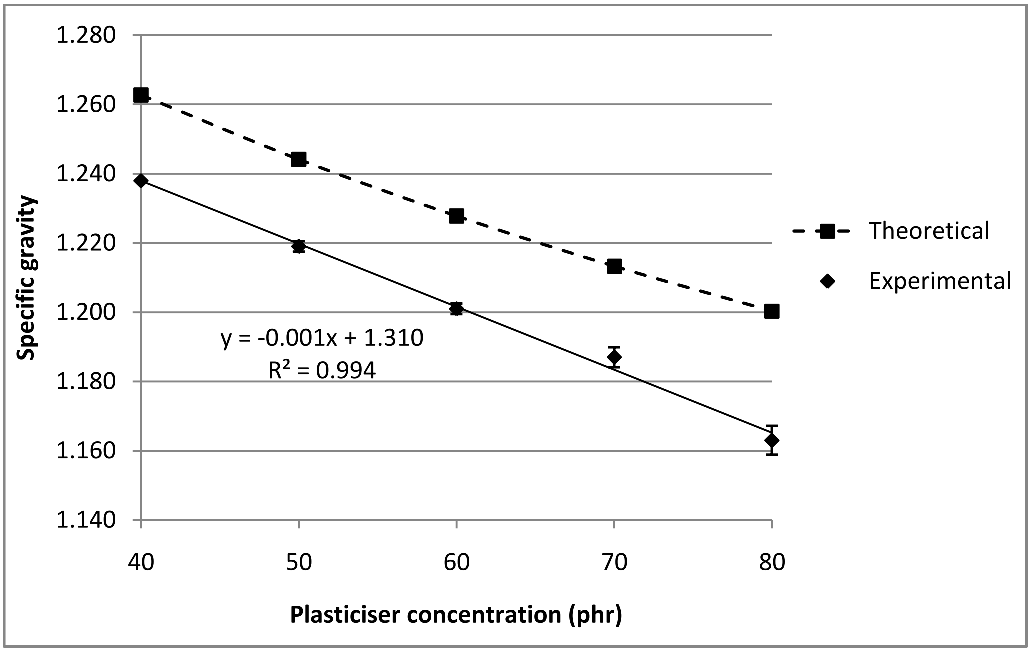


Figure 4.7: Specific Gravity of PVC Compounds Plasticised with DINP/DOA/ESO

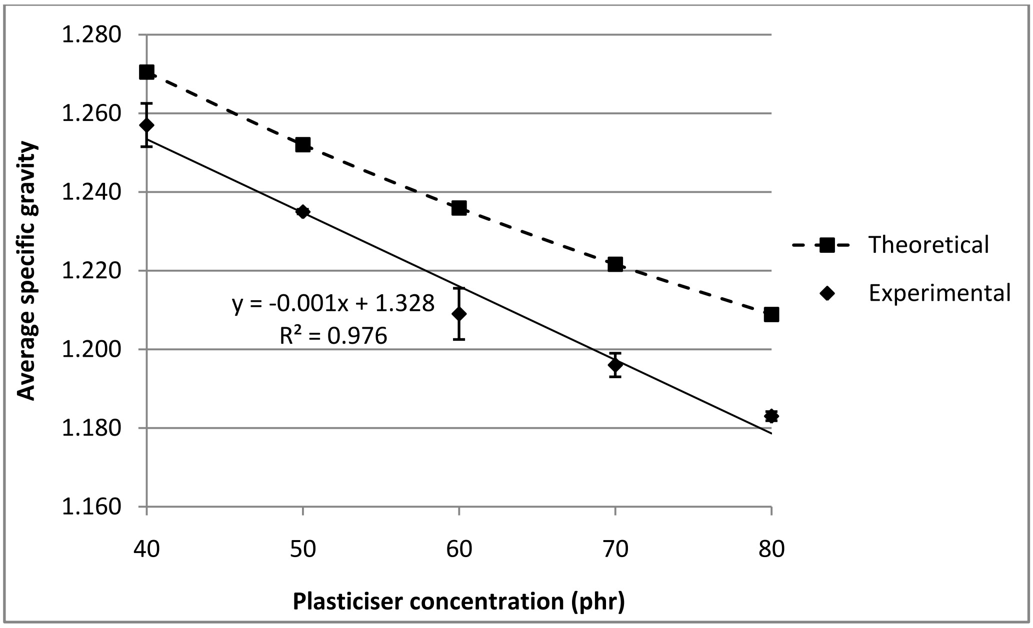


Figure 4.8: Specific Gravity of PVC Compounds Plasticised with DOTP/ESO

4.5 Scanning Electron Microscopy (SEM)

Figure 4.9 shows the fractured surface morphologies of DOA plasticised PVC compounds. The cracking and tearing structure appeared on fracture surface indicates that all the samples were pulled until break. At low plasticiser loading (Figure 4.9 (a) & (b)), the surface shows severe cracking but the contraction of polymer matrix is not readily observed. However, at high plasticiser loading (Figure 4.9 (c), (d) & (e)), obvious tearing structure was observed and the tore section was contracted into a wave form. These scenarios happen when the PVC compound elongate and try to contract back to the original position after the polymer breaks apart. During elongation, some regions undergo elastic deformation while some undergo plastic deformation. When the polymer contracts, only regions that undergo elastic deformation could return to original position; regions that undergo plastic deformation was unable to contract, resulting in wave like structure formation in the fracture surface.

Similar situation occurs in DINP/DOA/ESO-PVC (Figure 4.10) and DOTP/ESO-PVC (Figure 4.11) where cracking structure appears at low plasticiser loading level while tearing structure appears at high plasticiser concentration. Woven structure was observed in Figure 4.10 (e) and Figure 4.11 (e), showing that polymer matrix undergo contraction after breakage. As large amount of plasticisers were blended into the PVC resins, most of the polymer matrixes exhibit high flexibility and would undergo elastic deformation upon stretching. When the tensile stress was removed, the elongated polymer matrixes could contract back to the original position. Apart from that, some string like structure was shown in Figure 4.10 (d) and Figure 4.11 (c). This indicates that the polymer matrix undergoes plastic deformation during elongation and remains in that position even though the specimen had broken apart.

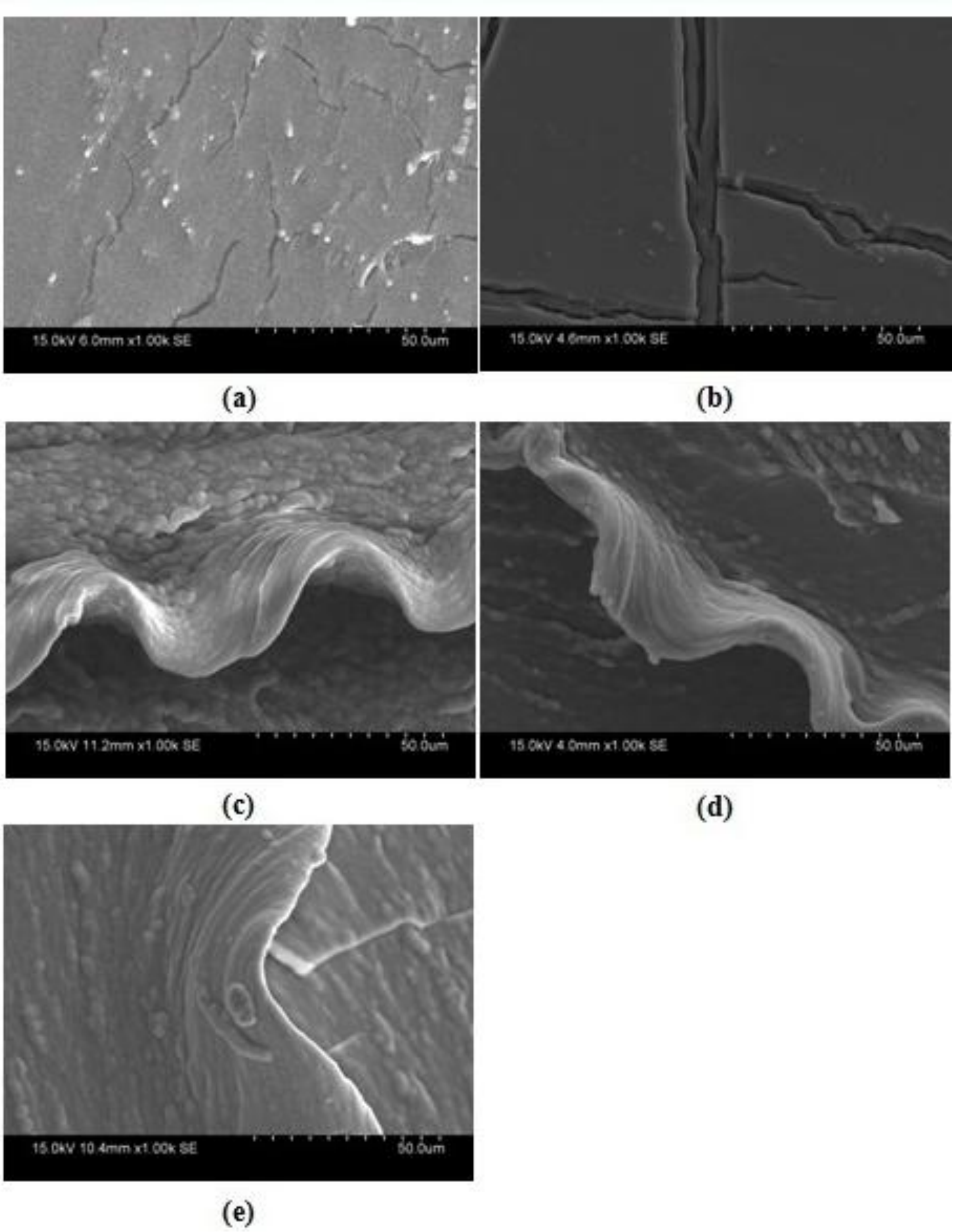


Figure 4.9: Morphologies of PVC Compounds Filled with DOA/ESO at the Point of Rupture from Tensile Strength Specimens for (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4 and (e) Sample 5 by SEM

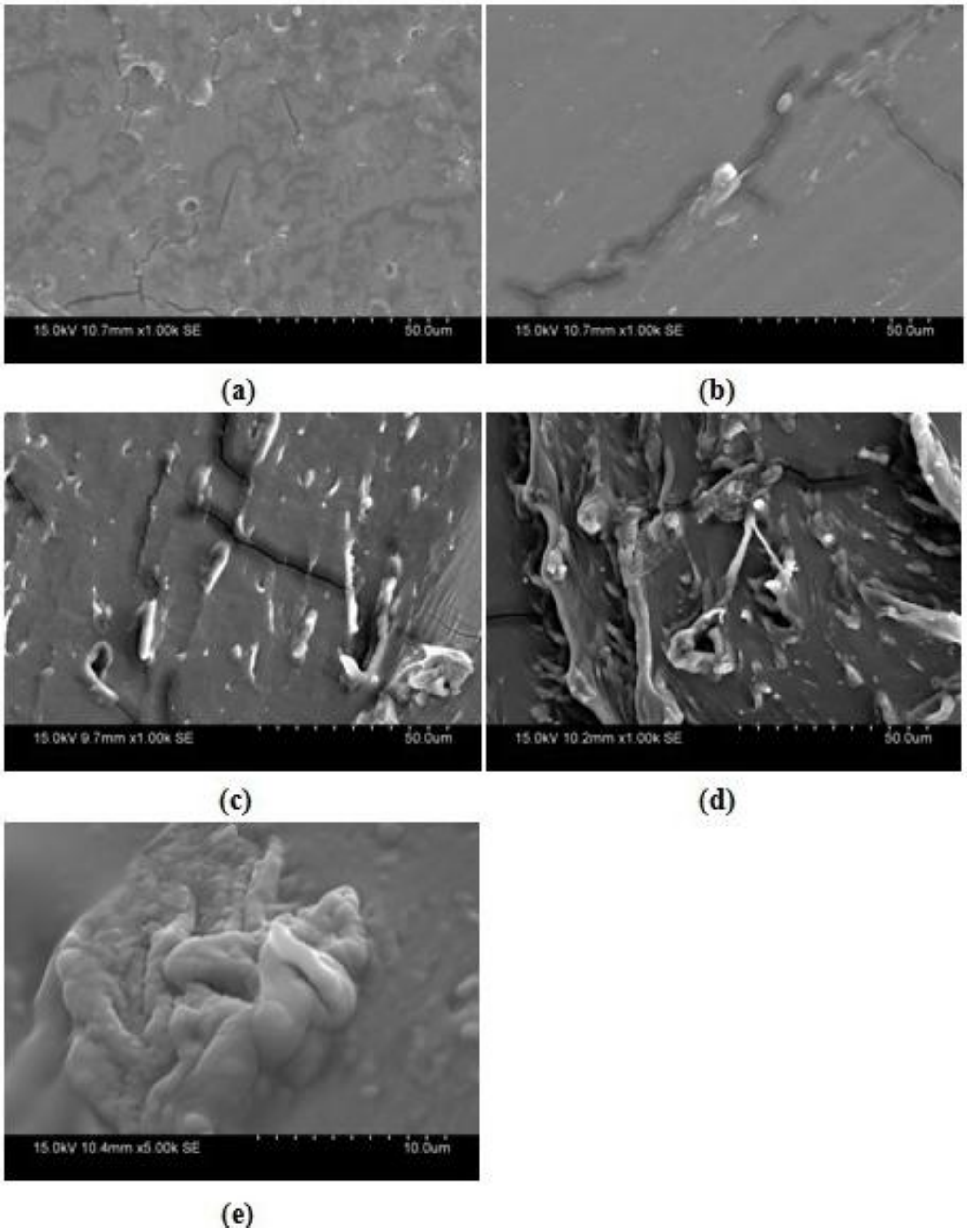
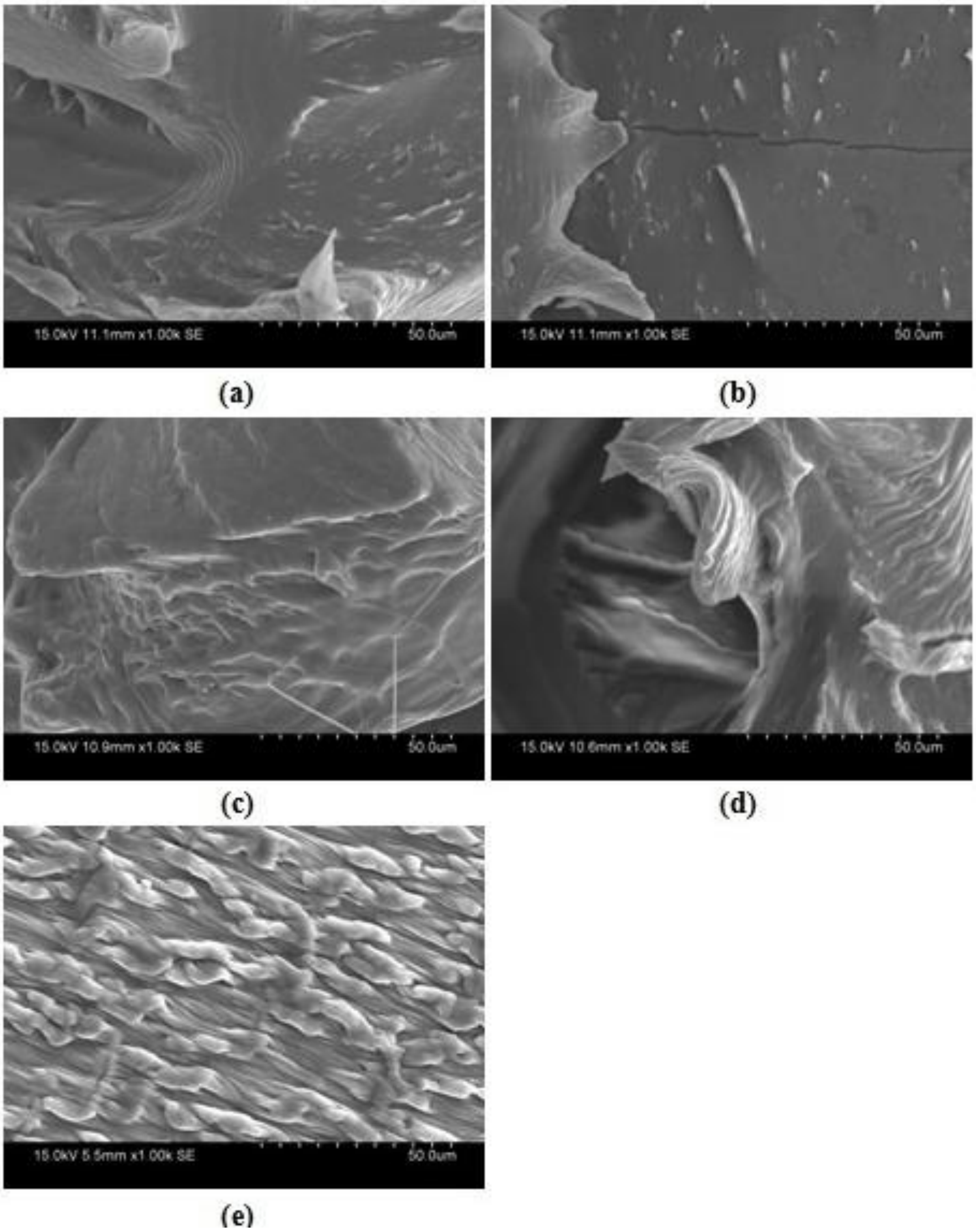


Figure 4.10: Morphologies of PVC Compounds Filled with DINP/DOA/ESO at the Point of Rupture from Tensile Strength Specimens for (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4 and (e) Sample 5 by SEM



(a) (b)

(c) (d)

(e)

Figure 4.11: Morphologies of PVC Compounds Filled with DOTP/ESO at the Point of Rupture from Tensile Strength Specimens for (a) Sample 1, (b) Sample 2, (c) Sample 3, (d) Sample 4 and (e) Sample 5 by SEM

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

In conclusion, addition of plasticisers had imposed pronounce effect on the mechanical and physical properties of polyvinyl chloride (PVC) compound. As the plasticisers' concentration increased, the tensile strength, Durometer hardness and specific gravity of PVC compound decreased while elongation at break increased. The tensile strength decreased almost linearly with increasing plasticiser loading for PVC compound plasticised with diisononyl phthalate, dicotyl adipate and epoxidised soybean oil (DINP/DOA/ESO-PVC) as well as dioctyl terephthalate and ESO (DOTP/ESO-PVC) but in a polynomial trend for dioctyl adipate and ESO added PVC compound (DOA/ESO-PVC). On the other hand, all plasticiser mixtures used in this study showed a polynomial trend of increment in elongation at break. For Durometer hardness and specific gravity, all three formulations showed linear reduction with increasing plasticiser concentration.

Among three types of plasticiser mixture investigated, DOA/ESO showed the highest plasticising efficiency in both tensile strength and Durometer hardness. The increment on elongation at break was also high but only limited to low plasticiser concentration. When the DOA concentration exceeded 50 phr, the changes in elongation at break became insignificant. The major drawback of formulation 1 was the relatively low compatibility of DOA with PVC resins. On the other hand, combination of DINP, DOA and ESO in formulation 2 gave intermediate efficiency in tensile strength and Durometer hardness. The elongation at break for DINP/DOA/ESO-PVC was lower than DOA/ESO-PVC at low plasticiser concentration (< 60 phr) but became higher than DOA/ESO-PVC when plasticiser loading level exceeded 60 phr. The compatibility with PVC resins was also slightly lower than DOTP but better than DOA. Lastly, the combination of DOTP and ESO showed lowest plasticising efficiency in tensile strength, elongation at break and Durometer hardness. Yet, DOTP was most compatible with PVC resins compared to DOA and DINP/DOA. By comparing three formulations investigated in this study, PVC compound blended with DINP, DOA and ESO (formulation 2) is most suitable for urine bag and urinary tubing application. Although the plasticising efficiency was lower than DOA, it is still acceptable as the compatibility with PVC resins was higher.

5.2 Recommendations

Homogeneity of PVC compounds was found important in determining the mechanical and physical properties. Thus, it is recommended to prepare the PVC compounds in pellet form through extrusion instead of two roll milling. Product from extrusion is generally more homogeneous and the data obtained during characteristic testing is more reliable. Besides that, specimens should have similar thermal history and impurities must be avoided to improve data accuracy. On the other hand, future study shall look into the structure of PVC compounds and investigate the migration tendency of plasticiser to produce high quality products for consumer use.

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APPENDIX

APPENDIX A: Data for tensile strength and elongation at break