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STRUCTURE-PROPERTY RELATIONSHIP OF POLYESTER AND PALM OIL POLYOLS AND THEIR EVALUATION IN SOLID POLYURETHANES

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By

TUAN NOOR MAZNEE BINTI TUAN ISMAIL

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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Understanding on the structure-property relationship between raw materials and the resultant polyurethane (PU) products is very crucial, especially for PU formulators. PU formulation is a trade secret, therefore, in development of PU products for specific target applications and performances, skill and expertise are required. To gain these skill and expertise, a lot of formulations need to be done which definitely involve cost and very time-consuming. However, these problems can be minimized with an availability of a systematic study on structure-property relationship between raw materials and their resultant PU products. Therefore, a systematic study on structure-property relationship of polyester and palm oil-based polyols in solid polyurethanes (SPUs) were conducted. SPUs made from polyester and palm oil-based polyols were characterized in terms of physico-mechanical and thermal properties as well as their morphologies. It was found that, in azelate polyols, resilience and durability of SPUs can be optimized by selecting azelate polyols with odd carbon number in the linear diols and by using shorter chain linear diols. In 1,4-butanediol-based polyester polyols, these properties can also be achieved by selecting polyester polyols from dicarboxylic acids (*n*-DCAs) with odd carbon numbers. It was also found that, the SPUs with maximized material strengths can be obtained from polyester polyols with even carbon numbers in both linear diols and *n*-DCAs. Phase interaction through formation of hydrogen bondings was the contributing factor to the properties of SPUs observed. For SPUs made from palm olein-based polyols, there were no significant changes in properties of SPUs observed, with regards to different types of reactants used during ring-opening reaction of epoxide groups. Thus, the findings could provide a guidance to PU formulators to choose the right raw materials to be used in their formulations. Through suitable choice of raw materials, a huge range of PU products could be made. Therefore, the findings from this study

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could have practical significance in the selection and synthesis of polyester and palm oil-based polyols for PU applications.

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HUBUNGAN DI ANTARA STRUKTUR-SIFAT POLIOL POLIESTER DAN POLIOL SAWIT, DAN PENILAIANNYA DALAM POLIURETANA PEJAL

Oleh

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Memahami hubungkait di antara struktur-sifat bahan-bahan asas di dalam formulasi poliuretana adalah sangat penting. Formulasi poliuretana adalah rahsia perniagaan, oleh itu, di dalam pembangunan produk poliuretana untuk kegunaan yang spesifik dan berprestasi tinggi, kepakaran dan kemahiran individu diperlukan. Kepakaran dan kemahiran ini boleh diperolehi melalui pengalaman dengan penghasilan banyak formulasi-formulasi poliuretana yang menjurus kepada peningkatan kos dan tempoh masa yang lama. Walau bagaimana pun, masalah ini boleh diminimumkan jika ada satu panduan yang boleh digunakan untuk memilih bahan asas yang betul bagi membangunkan produk poliuretana mengikut spesifikasi tertentu. Oleh yang demikian, kajian secara sistematik ke atas hubungkait di antara struktur poliol poliester dan poliol sawit ke atas sifat poliuretana pejal telah dilakukan untuk memenuhi keperluan tersebut. Poliuretana pejal yang dihasilkan daripada poliol poliester and poliol sawit telah dicirikan sifat-sifat fiziko-mekanikal dan terma serta morfologinya. Didapati, sifat lantunan dan tahan lasak poliuretana pejal boleh dioptimumkan melalui pemilihan poliol azelat dengan diol bernombor karbon ganjil dan diol berantai karbon pendek. Bagi poliol poliester berasaskan 1,4-butandiol, sifat-sifat tersebut boleh dicapai dengan memilih asid dikarboksilik bernombor karbon ganjil. Untuk menghasilkan poliuretana pejal dengan kekuatan bahan yang maksimum, poliol poliester dengan nombor karbon genap bagi kedua-dua bahagian diol dan asid dikarboksilik hendaklah digunakan. Interaksi di antara fasa melalui pembentukan ikatan hidrogen telah mempengaruhi sifat-sifat poliuretana pejal. Bagi poliuretana pejal yang dihasilkan daripada poliol sawit olein, tiada perubahan ketara diperhatikan dengan perbezaan jenis reaktan yang digunakan di dalam penghasilan poliol sawit. Melalui pemilihan poliol dan isosianat yang sesuai, pelbagai jenis produk poliuretana boleh dihasilkan. Oleh itu, penemuan hasil kajian ini secara praktikal boleh digunakan di dalam pemilihan dan sintesis poliol poliester dan poliol sawit untuk menghasilkan produk poliuretana mengikut kegunaannya.

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The thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF SCHEMATICS

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LIST OF ABBREVIATIONS

AA	Adipic acid
AFM	Atomic force microscopy
AOCS	American Oil Chemists' Society
AZ	Azelaic acid
AZBDO	Poly(butylene azelate)
AZEG	Poly(ethylene azelate)
AZHDO	Poly(hexamethylene azelate)
AZNPG	Poly(dimethylpropylene azelate)
AZPDO	Poly(propylene azelate)
AZPG	Poly(methylethylene azelate)
AZPTDO	Poly(pentamethylene azelate)
BDAA	Poly(butylene adipate)
BDAZ	Poly(butylene azelate)
BDAZAA	Poly(butylene azelate-*co*-butylene adipate)
BDAZSA	Poly(butylene azelate-*co*-butylene succinate)
BDGA	Poly(butylene glutarate)
BDPA	Poly(butylene pimelate)
BDSA	Poly(butylene succinate)
BDSebA	Poly(butylene sebacate)
BDSubA	Poly(butylene suberate)
$BF_3.Et_2O$	Boron trifluoride diethyletherate
Bio-1,3-PDO	Bio-based 1,3-propanediol
CAGR	Compound annual growth rate
CASE	Coatings, adhesives, sealants and elastomers

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ChE	Chain extender
DAG	Diglycerides
DEG	Diethylene glycol
DIC	Diisocyanates
DMA	Dynamic mechanical analysis
DRI	Differential refractive index
DSC	Differential scanning calorimetry
E-FAME	Epoxidized fatty acid methyl ester
EG	1,2-Ethanediol
ELSD	Evaporative light scattering detector
EO	Ethylene oxide
EPOo	Epoxidized palm olein
ESBO	Epoxidized soybean oil
FAME	Fatty acid methyl ester
FTIR	Fourier transform infra-red
FWHM	Full width at half maximum
GA	Glutaric acid
GC	Gas chromatograhpy
GC-FID	Gas chromatograhpy-flame ionization detector
GPC	Gel permeation chromatography
HCl	Hydrochloric acid
HDI	1,6-Hexamethylene diisocyanate
HPLC	High performance liquid chromatography
HS	Hard segment
H_2O_2	Hydrogen peroxide
MDI	Methylenediphenyl diisocyanates

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MEK	Methyl ethyl ketone
MPOB	Malaysian Palm Oil Board
MW	Molecular weight
M_ns	Number-average molecular weights
MWD	Molecular weight distribution
M_ws	Weight-average molecular weights
NaCl	Sodium chloride
NaOH	Sodium hydroxide
Na_2CO_3	Sodium carbonate
n-DCAs	Linear dicarboxylic acids
NDI	1,5-Naphthalene diisocyanate
NPG	2,2’-Dimethyl-1,3-propanediol
OOC	Oxirane oxygen content
PA	Pimelic acid
PBA	Poly(butylene adipate)
PBS	Poly(butylene succinate)
PCL	Polycaprolactone
PDI	Polydispersity index
PDT	3,3’-[Methylene (1,4-phenylenemethylenethio)] dipropan-1-ol
PG	1,2-Propanediol
PO	Propylene oxide
POE	Poly(ethylene oxide)
POo	Refined, bleached, deodorized palm olein
POoP BDO	Epoxidized palm olein ring-opened with 1,4-butanediol
POoP EG	Epoxidized palm olein ring-opened with 1,2-ethanediol

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POoP H	Epoxidized palm olein ring-opened with water
POoP HDO	Epoxidized palm olein ring-opened with 1,6-hexanediol
POoP M	Epoxidized palm olein ring-opened with methanol
POoP PDO	Epoxidized palm olein ring-opened with 1,3-propanediol
POoP PG	Epoxidized palm olein ring-opened with 1,2-propanediol
POoP polyols	Palm olein polyols
POoP PTDO	Epoxidized palm olein ring-opened with 1,5-pentanediol
PolyFAME BDO	Epoxidized fatty acid methyl ester ring-opened with 1,4- butanediol
PolyFAME EG	Epoxidized fatty acid methyl ester ring-opened with 1,2-ethanediol
PolyFAME H	Epoxidized fatty acid methyl ester ring-opened with water
PolyFAME HDO	Epoxidized fatty acid methyl ester ring-opened with 1,6-hexanediol
PolyFAME M	Epoxidized fatty acid methyl ester ring-opened with methanol
PolyFAME PDO	Epoxidized fatty acid methyl ester ring-opened with 1,3-propanediol
PolyFAME PG	Epoxidized fatty acid methyl ester ring-opened with 1,2-propanediol
PolyFAME polyols	Fatty acid methyl ester polyols
PolyFAME PTDO	Epoxidized fatty acid methyl ester ring-opened with 1,5-pentanediol
PU	Polyurethane
SA	Succinic acid
S-AZBDO	Solid polyurethane made from poly(butylene azelate)
S-AZEG	Solid polyurethane made from poly(ethylene azelate)

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S-AZHDO	Solid polyurethane made from poly(hexamethylene azelate)
S-AZNPG	Solid polyurethane made from poly(dimethylpropylene azelate)
S-AZPDO	Solid polyurethane made from poly(propylene azelate)
S-AZPG	Solid polyurethane made from poly(methylethylene azelate)
S-AZPTDO	Solid polyurethane made from poly(pentamethylene azelate)
S-BDAA	Solid polyurethane made from poly(butylene adipate)
S-BDAZ	Solid polyurethane made from poly(butylene azelate)
S-BDAZAA	Solid polyurethane made from poly(butylene azelate-*co*-butylene adipate)
S-BDAZSA	Solid polyurethane made from poly(butylene azelate-*co*-butylene succinate)
S-BDGA	Solid polyurethane made from poly(butylene glutarate)
S-BDO	Solid polyurethane made from POoP BDO
S-BDPA	Solid polyurethane made from poly(butylene pimelate)
S-BDSA	Solid polyurethane made from poly(butylene succinate)
S-BDSebA	Solid polyurethane made from poly(butylene sebacate)
S-BDSubA	Solid polyurethane made from poly(butylene suberate)
SebA	Sebacic acid
SEC	Size exclusion chromatography
S-EG	Solid polyurethane made from POoP EG
S-H	Solid polyurethane made from POoP H
S-HDO	Solid polyurethane made from POoP HDO
S-M	Solid polyurethane made from POoP M
S-PDO	Solid polyurethane made from POoP PDO

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S-PG	Solid polyurethane made from POoP PG
S-PTDO	Solid polyurethane made from POoP PTDO
SPU	Solid polyurethane
SS	Soft segment
SubA	Suberic acid
TAG	Triglycerides
TDI	2,4-Toluene diisocyanate
THF	Tetrahydrofuran
TMDI	2,2',4-Trimethyl-1,6-hexamethylene diisocyanate
TPUs	Thermoplastic urethanes
VPO	Vapor pressure osmometry
WAXD	Wide angle X-ray diffraction
1,3-PDO	1,3-Propanediol
1,4-BDO	1,4-Butanediol
1,5-PTDO	1,5-Pentanediol
1,6-HDO	1,6-Hexanediol
4,4'-MDI	4,4'-Methylene diphenyldiisocyanate

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CHAPTER 1

INTRODUCTION

1.1 Background of study

In general, solid polyurethanes (SPUs) are segmented linear block copolymers formed by alternating hard and soft segments. The hard segment (HS) is composed of diisocyanate moiety, urethane groups and chain extender(s), displaying strong hydrogen bonding between urethane groups, which form physical cross-linked networks, while the soft segment (SS) consists of a flexible polyol chain (Costa *et al*., 2015; Cruz & Viana, 2015; Chattopadhyay *et al*., 2006; Velankar & Cooper, 1998).

The great interest on SPUs is due to their functional properties that can be tuned by the choice of raw materials (polyol, isocyanate and chain extender), preparation and processing conditions. The variability of the composition of polyol (SS) such as polyether, polyester and polycarbonate, and the chain length of the SS; chemical nature of diisocyanates such as aromatic, aliphatic and cycloaliphatic, and a wide range of chain extenders, short chain diols such as 1,3-propanediol (1,3-PDO), 1,4-butanediol (1,4-BDO), 1,6-hexanediol (1,6-HDO) and diamines, together with the possibility to modify the preparation procedure, offer an almost infinite variety in end-use properties of SPUs (Norhayati *et al*., 2016; Tharcis *et al*., 2016; Costa *et al*., 2015; Saralegi *et al*., 2013; Rinaldi *et al*., 2010; Oprea, 2009; Xie *et al*., 2009).

Thermodynamic phase separation or interaction between the HS and the SS dictates many properties of SPUs. The HS acts as physical crosslinks which gives the material strength, stiffness and upper use temperature. The SS imparts elastomeric properties such as resilience, toughness, low-temperature properties and resistance to water and oils (Beuhler *et al*., 2015; Cruz & Viana, 2015; Beuhler, 2014; Drobny, 2007).

Of all the SPU materials, polyurethane (PU) elastomers have gained the largest market acceptance. PU elastomers have found wide applications in virtually every industry because of their very special properties. The most important of which are their:

- High elasticity over the entire hardness range
- Flexibility over a wide temperature range
- Good weather resistance
- Good resistance to oil, grease and many solvents' excellent wear resistance and
- A high Young's modulus compared with rubbers of a similar hardness.

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PU elastomers are used widely in the manufacture of gaskets for both hydraulic and pneumatic apparatus such as piston and cylinder gaskets. Materials used in this application would have Shore hardness in the range of 85 Shore A to 60 Shore D. This application requires wear resistance, rigidity and resistance to oil and grease. In this case, PU elastomers made from polyester polyols are of the better option as it shows excellent compatibility with hydraulic fluids based on mineral oils, as evidenced by the low swelling rates in these types of media (Drobny, 2007; Oertel, 1993). Commonly used polyols and their general trends in properties (both polyols and their corresponding PU elastomers) are shown in Table 1.1.

Table 1.1: Thermal properties of important polyols[1] and their corresponding PU elastomers[2] (Drobny, 2007)

Polyols	**Thermal properties of polyols**		**Properties of PU elastomers**	
	***T_e*, °C**	***T_m*, °C**	***T_e*, °C**	**Hydrolytic stability**
Poly(ethylene adipate)	-46	52	-25	Fair
Poly(butylene adipate)	-71	56	-40	Good
Poly(ethylene-butylene adipate)	-60	17	-30	Fair/Good
Poly(hexamethylene-2,2'-dimethylpropylene adipate)	-57	27	-30	Good
Polycaprolactone	-72	59	-40	Good
Poly(diethylene glycol adipate)	-53	-	-30	Poor
Poly(hexanediol-1,6 carbonate) diol	-62	49	-30	Very good
Poly(oxytetramethylene) glycol	-100	32	-80	Very good

Note: [1]Molecular weight 2000 g mol^{-1}, [2]Hardness approx. 85 Shore A, T_e – Lower end of glass transition range.

Factors such as molecular weight (Brokenbrow *et al*., 1971 and Costa *et al*., 2015), chemical nature of repeating unit (Xu *et al*., 2015; Mohammadnia *et al*., 2012; Drobny, 2007; Zhang & Feng, 2004), HS and SS concentrations (Costa *et al*., 2015; Drobny, 2007; Chattopadhyay *et al*., 2006) and incorporation of fillers (Cruz & Viana, 2015; Drobny, 2007) have important influenced on morphology, mechanical, and thermal properties of polyurethanes (PUs). Most of the studies on the above-mentioned factors were conducted on SPUs or PU elastomers because of their well-defined chemical structure (Hepburn, 1992), which effectively and in most cases, directly illustrates the structure-property relationship.

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SPUs can be obtained *via* a one-shot or two-shot method. In the one-shot method, all reactants (diisocyanate, polyol, chain extender), at the desired stoichiometric ratios are mixed together and then, the reaction mixture is poured into the mold where the crosslinking reaction occurs. In the two-shot method, which is also called the prepolymer method, diisocyanate is reacted with oligomer (*e.g.* polyester and polyether polyols) to obtain prepolymer. The resulting prepolymer is terminated by the isocyanate groups. After that, the prepolymer is reacted with chain extender which is usually short chain diols and diamines. Both methods possess advantages and disadvantages. The one-step polymerization (one-shot method) gives more random block polymers as compared to two-step process (Datta & Kasprzyk, 2018; Prisacariu, 2011). For prepolymer method, linear oligomer (*e.g.* polyester polyol diol) with an average functionality close to 2 is usually used (Drobny, 2007).

In this study, one-shot method was used because this method can be applied to both polyester and palm oil-based polyols since the palm oil-based polyols are not linear in structures and they have relatively high functionality.

1.1.1 Polyester polyols and solid polyurethanes

Polyester polyols are widely used in thermoplastic PU elastomers (Ionescu, 2005). They are typically produced *via* polyesterification reaction between diols and dicarboxylic acids. The most common polyester polyols are adipate polyols produced from the polyesterification reaction of adipic acid with short chain diols (Bacaloglu *et al*., 1998; Chang & Karalis, 1993; Saunders & Frisch, 1962).

Depending on the types of diols used in the polyesterification reaction, adipate polyols can be crystallizable (symmetrical) or non-crystallizable (non-symmetrical) as indicated in Table 1.2.

Table 1.2: Adipate polyols produced from different types of diols
(Sendijarevic, 2008)

Crystallizable (Symmetrical)	Non-crystallizable (Non-symmetrical)
Poly(hexamethylene adipate) or 1,6-hexanediol adipate	Poly(methylethylene adipate) or 1,2-propanediol adipate
Poly(butylene adipate) or 1,4-butanediol adipate	Poly(dimethylpropylene adipate) or neopentyl glycol adipate
Poly(ethylene adipate) or 1,2-ethanediol adipate	Poly(propylene adipate) or 1,3-propanediol adipate

With increasing demand and awareness on green and bio-based products, development of bio-based thermoplastic PU products, such as from succinate, azelate, and sebacate polyols, are highly desirable. Bio-based polyester polyols could be obtained from renewable resources either through biotechnological

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process (succinic and adipic acids) (Pellis *et al*., 2016), or chemical pathways (azelaic and sebacic acids) (Köckritz & Martin, 2011; Tuszynski & Bessette, 2008). Oleic acid as a feedstock for the production of azelaic acid has an economic feasibility due to abundant supply of oleic acid from vegetable oils, especially palm oil (Kushairi *et al*., 2018).

Many researchers have focused on the effect of SS type and length, HS type and concentration, hard domain crystallinity, and the extent of microphase segregation on structure-property relationships in segmented PUs (Tharcis *et al*., 2016; Fernández-d'Arlas *et al*., 2014; Xie *et al*., 2012; Bagdi *et al*., 2011; Kojio *et al*., 2010). Structure-property relationships of polyester polyols prepared from one or mixture of dicarboxylic acids and with different diols have also been extensively evaluated (Xu *et al*., 2015; Sonnenschein *et al*., 2010; Zhang & Feng, 2004). However, systematic study on SPUs based on polyester polyols at controlled molecular weight is still limited. Therefore, there is a need to establish a comprehensive structure-property correlation in polyester polyols and SPUs in order to speed up the development of PU products especially for specific target applications. In addition, PU formulation is a trade secret.

1.1.2 Palm oil-based polyols and solid polyurethanes

Vegetable oils have attracted increasing attention as one of the most important platform chemicals for the chemical industry due to their availability, relatively low cost and environmental sustainability (Chen *et al*., 2015; Caillol *et al*., 2012; Lligadas *et al*., 2010). Vegetable oils, mainly triglycerides (TAG) constituted by glycerol and three fatty acid chains, commonly contain unsaturated carbon-carbon double bonds (-C=C-) or alkene groups that are available for modification to form more reactive functional groups (Omonov *et al*., 2016; Chen *et al*., 2015; Desroches *et al*., 2012). Many modifications of vegetable oils have been described including epoxidation, carbonation, esterification and/or transesterification, ozonolysis, *etc*. (Omonov *et al*., 2016; Desroches *et al*., 2012). There are several approaches available for the epoxidation of the alkene groups to make epoxide groups, however, the most widely used method is the classical epoxidation reaction proposed by Prileschajew (Omonov *et al*., 2016). It takes place in two stages, whereby, in the first stage, peroxy acid is formed and in the second stage, the peroxy acid reacts with alkene groups to form epoxide groups. Indeed, epoxidation of vegetable oils is an industrial process, mature, well controlled and less expensive (Omonov *et al*., 2016; Caillol *et al*., 2012).

Palm oil like other vegetable oils, is made up of hydrocarbons (fatty acid chains) attached to a glycerol back bone through ester linkages. The hydrocarbon moieties of the TAG molecules are made up of saturated and unsaturated carbon chain. Palm oil itself is not reactive to be used as polyols, therefore, hydroxyl group need to be introduced into molecular structure of palm oil. This can be done through modification of alkene groups or ester group (Desroches *et al*., 2012; Lligadas *et al*., 2010; Sharma & Kundu, 2006).

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The development of palm oil-based polyols in Malaysia was first started by Malaysian Palm Oil Board (MPOB) in early 1990s. Epoxidation and alcoholysis are two main chemical reactions used to produce polyols, which involve modification of alkene groups of palm oil. Severals feedstock have been used to produce polyols such as palm oil, refined, bleached, deodorized palm olein (POo), used frying oil, oleic acid and winter grade biodiesel (fatty acid methyl ester (FAME)). Most of the polyols processes have been patented, for examples, polyols prepared from palm oil has been patented in Malaysia with a patent number MY-114189-A. Meanwhile, polyols made from refined, bleached, deodorized palm olein, used frying oil and oleic acid have been patented in United States with patent numbers US7932409, US8501826 and US7629478, respectively.

Depending on their feedstock, palm oil-based polyols with variable functionalities, hydroxyl numbers and viscosities could be produced. Research and developmental work conducted by MPOB indicated that the palm oil-based polyols could be used in rigid PU foams (Tuan Noor Maznee *et al*., 2001) as insulation materials, in flexible PU foams (Srihanum *et al*., 2017) as bedding and mattresses, cushioning foams and as coatings and adhesives (Mohd Norhisham *et al*., 2017). The PU coatings and adhesives are of SPUs.

Despite all the palm-based PU products developed so far, there is a need for a comprehensive study on properties of SPUs made from palm oil-based polyols in order to better understand the structure-property relationship of palm-based PU products. This understanding will help in speed up the development of palm-based PU products, which have commercial viability.

1.2 Problem statement

PUs are very versatile polymeric materials with a wide range of applications. It has been used in all aspects of our daily life. PUs can be found in furniture and mattresses, transportation, building construction, technical insulation, automotive, footwear, *etc*. (Oertel, 1962). Versatility of PUs is due to the unique chemistry of isocyanates which react with compound containing active hydrogen. Understanding on the structure-property relationship between raw materials and the resultant PU products is very crucial, especially for PU formulators. PU formulation is a trade secret, therefore, in development of PU products especially for specific target applications and performances, skill and expertise are required. To gain these skill and expertise, a lot of formulations need to be done which definitely involve cost and very time-consuming. However, these problems can be minimized with an availability of a systematic study on structure-property relationship between raw materials and their resultant PU products. Therefore, a systematic study on structure-property relationship of polyester and palm oil-based polyols in SPUs was conducted.

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1.3 Objectives of study

The main objectives of the study are:

i. To synthesize and to characterize azelate polyols based on azelaic acid and diols of different chain lengths and structures (both linear and branched diols),
ii. To synthesize and to characterize 1,4-butanediol-based polyester polyols using 1,4-butanediol and dicarboxylic acids of different chain lengths,
iii. To synthesize and to characterize palm oil-based polyols using refined, bleached, deodorized palm olein and fatty acid methyl ester with different types of reactants,
iv. To prepare and to characterize solid polyurethanes using polyester and palm olein-based polyols.

1.4 Overview of thesis

The present thesis aims to understand, by means of systematic study, the effects of varying chemical composition in polyols on model SPUs.

In this thesis, the study was divided into two main parts: the first part involved preparation of polyester polyols from diols and dicarboxylic acids of various chain lengths, followed by evaluation of the obtained polyester polyols in SPUs; and the second part involved preparation of palm oil polyols from ring-opening of epoxide groups with reactants of different types, followed by evaluation of the obtained palm oil polyols in SPUs. Results were related to the structure-property correlation, on the basis of evidence from Fourier transform infra-red (FTIR), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), physico-chemical, mechanical and dynamic measurements, atomic force microscopy (AFM), wide angle X-ray diffraction (WAXD) and solvent resistance test.

The thesis is organized into 8 chapters. Chapter 1 describes an introduction to SPUs, polyester and palm oil-based polyols as a background of the study, followed by a problem statement and objectives of study. Chapter 2 represents literature review on general aspects of polyurethane chemistry, types of polyurethanes, types of polyols, structure-property correlation in polyurethanes and applications of SPUs. In addition, general overview of polyurethanes market is briefly described in Chapter 2. Materials and methods used in the preparation and characterization of polyester and palm oil polyols and their SPUs are presented in Chapter 3.

Chapter 4 discusses structure-property correlation of azelate polyols prepared from azelaic acid and diols of various chain lengths (C2 to C6), including branched structure diols (C3 and C5) and their evaluation in SPUs. SPUs were

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prepared by reacting the azelate polyol with 4,4’-methylene diphenyldiisocyanate (4,4’-MDI). Results were discussed in terms of structural studies using AFM and WAXD revealing particularities on the SPUs morphology, thermal behavior of the SPUs were investigated using DSC and DMA. Mechanical performance of SPUs is strongly affected by higher-ordered structure of the HSs (isocyanate-chain extender) on the macromolecular chain. Crystallizable polyol chains (SSs) could also affect the mechanical performance of the SPUs. Mechanical properties of SPUs were determined using mechanical analyzer (Instron). Deconvulated FTIR was used to reflect *inter*molecular interaction in SPUs. In Chapter 5, 1,4-butanediol (1,4-BDO)-based polyester polyols were prepared from 1,4-BDO and linear dicarboxylic acid (*n*-DCA) of various chain lengths (C4 to C10), followed by evaluation of the prepared polyester polyols in SPUs. Structure-property correlation of the 1,4-BDO-based polyester polyols and SPUs were evaluated similarly as in Chapter 4. In addition, SPUs made from co-polyester polyols prepared using mixture of *n*-DCAs were also investigated. The use of mixture of *n*-DCAs and branched diols in the preparation of polyester polyols have widen the properties of the polyester polyols, which in turn, have broaden the properties of SPUs. This will open a broad spectrum for PU formulators to tailor-make the PU products according to their specific target applications.

Chapter 6 describes palm olein-based polyols made from ring-opening reaction of epoxide groups with different types of reactants (water, monol and diols). In acid-catalyzed condition, ring-opening reaction of epoxide groups favored oligomerization as witnessed in chromatograms of gel permeation chromatography (GPC). SPUs prepared using palm olein-based polyols were investigated similarly as SPUs in Chapters 4 and 5. In Chapter 7, fatty acid methyl ester polyols were prepared using the same epoxide ring-opening reaction with the same reactants used in the preparation of palm olein polyols. Similarly, formation of oligomers were observed. The prepared polyols were also used to make SPUs. However, the prepared SPUs exhibited cracked throughout the specimen due to high HS concentration. Therefore, these SPUs could not be used for further evaluation.

Finally, in Chapter 8, recommandations for future work are addressed. This study has shown that polyester polyols with a wide range of properties could be prepared by changing the diols and *n*-DCAs chain lengths, including branched diols and mixture of *n*-DCAs. With a wide range of properties of polyester polyols, PU with a broad range of applications could be produced. On the other hand, for palm olein-based polyols, no significant difference in the properties of the SPUs were observed when different types of reactants used during ring-opening reaction of epoxide groups. This finding could be useful, from commercial perspective, as a guideline to choose the most economical polyol to be produced. In regards to fatty acid methyl ester polyols, these polyols can be reacted with different types of isocyanates to produce PU products. Previous study showed that the fatty acid methyl ester polyols have potential applications in soft elastomers and pressure sensitive adhesives (Mohd Norhisham *et al*., 2017).

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Tuan Noor Maznee Tuan Ismail was born in Bachok, Kelantan on 21st January 1977. She completed her secondary education at Sekolah Menengah Putri Saadong, Bukit Marak, Kota Bharu, Kelantan (1990), then, at MARA Junior Science College Pasir Tumboh, Kota Bharu, Kelantan (1991-1992) and after that at MARA Junior Science College Muar, Muar, Johor (1993-1994). After completing her secondary education, she continued her education at Matriculation Center of MARA Science College, Seremban, Negeri Sembilan (1995). In 1999, she obtained her Bachelor of Science degree in Chemistry from National University of Malaysia. She further obtained a Master of Science degree from University Putra Malaysia in 2013 in the area of Oleochemistry in which fatty hydrazides were synthesized enzymatically using palm olein. She started her career as a research officer at Palm Oil Research Institute of Malaysia (PORIM, now known as MPOB) in December 1999 on a contract basis and in May 2001, she was appointed as a permanent research officer in Advanced Oleochemical Technology Division (AOTD), MPOB. In 2010 till present, she has been appointed as a group leader for Polymer and Composite Group of AOTD. Her research interests include syntheses of palm oil-based polyols, polyester polyols, fatty hydrazides and development of polyurethane foams and non-foams products. Since 2001, she has authored 8 publications and co-authored 17 publications in peer reviewed journals, and 6 patents (both granted and pending approval). She has also received more than 15 awards, locally and internationally, in the areas of polyols and polyurethanes.

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