

SYNTHESIS AND CHARACTERIZATION OF AMIDE BASED PALM OIL
POLYOL VIA RING OPENING REACTION

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A thesis submitted in fulfilment of
the requirements for the award of the degree of
Doctor of Philosophy (*Polymer Engineering*)

School of Chemical and Energy Engineering
Faculty of Engineering
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OCTOBER 2018

Husband, Mohd Ikhwan Ibrahim - for the never ending supports. The most outstanding person throughout this PhD journey.

Daughters, Aisyah and Maryam- precious gift from Allah.

Families, best supporter as per request.

ACKNOWLEDGEMENT

Alhamdulillah, all praise to Allah for all His Blessings that give me the strength to finish up this thesis. Without the will of Allah, I will not be able to complete this thesis. All praise to HIM, again and again, the Most Merciful, The Knower of All, The Responder to all my caller. Truly, without the permission of HIM, this manuscript will not be complete as it is.

I would also appreciate my main supervisor, Dr Rohah A. Majid, my co-supervisor; Assoc. Prof Dr Abdul Razak Rahmat and Dr Jamarosliza Jamaluddin for their comments, guidance and idea in helping me to develop the structure of this manuscript. Also, for their motivational support every time I felt disappointed with my progress. The appreciation also goes to KPT and UMS for my UMS-SLAB scholarship.

I am also indebted to my families for their supports and understanding. Not to forget, my UMS friends (Rahmawati, Norliza, Izkiah and Ramziah) and my lab-mates for moral supports and some technical guidance. Last but not least, to the FKT's lab assistant team that assist me in my sample analysis.

Special thanks to Siti Marhaida and Siti Khairunnisah for helping me in the process of submission this manuscript to the postgraduate office. May Allah bless you two.

ABSTRACT

The use of epoxidized palm oil (EPO) as an intermediate for polyol production has been the main interest due to the ability of the epoxy group to react with various nucleophiles such as hydroxyl and amines. However, there are relatively limited numbers of articles that discuss the mechanism of ring opening reaction of EPO with nucleophiles. In this study, the epoxy ring of EPO underwent ring opening reaction using isopropanolamine (IPA) as the nucleophile and boron trifluoride ethanol complex as catalyst. The mechanism of this reaction was following unimolecular nucleophilic substitution reaction (S_N1) based on detail analysis using Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR). Reaction time, reaction temperature, catalyst amount and molar ratio of EPO:IPA were varied in order to investigate the efficiency of IPA as the ring opening reagent. It was found that the ring opening reaction occurred after 6 hours of reaction at 60°C with 1 mL of boron trifluoride ethanol complex catalyst and at the ratio of 1:3 EPO:IPA. However, small trace of unopened epoxy ring was detected by FTIR and NMR analyses at 824-830 cm^{-1} and 2.89 ppm. Further analysis with FTIR and NMR revealed that IPA preferred to attack the ester linkages over the epoxy ring, thus producing amide polyols as the main product. Findings from mass spectroscopy analysis and gel permeation chromatography showed that amide polyols had shorter chain length with the molecular weights ranging from 400 to 600 Da with broad distribution. From hydroxyl value analysis, amide polyols have functionality of 2, thus suitable to be used as precursor in many chemical reactions. Further investigation with thermogravimetric analysis showed that amide polyols had thermal decomposition at temperatures of 600°C, indicating that they can be used at high-temperature reactions.

ABSTRAK

Penggunaan minyak sawit teroksidasi (EPO) sebagai bahan perantara untuk penghasilan polioliol antara kajian yang menjadi perhatian kerana kebolehan kumpulan epoksida untuk bertindak balas dengan pelbagai jenis nukleofil seperti alkohol dan amina. Bagaimana pun, artikel yang membincangkan mekanisme tindak balas pembukaan gelang EPO oleh nukleofil adalah amat terhad. Kajian ini, gelang epoksida EPO mengalami tindak balas pembukaan gelang menggunakan isopropanolamina (IPA) sebagai nukleofil dan kompleks etanol boron triflorida sebagai pemangkin. Mekanisma tindak balas ini mematuhi tindak balas penggantian nukleofil unimolekul (S_N1) berdasarkan analisis terperinci spektroskopi infra merah jelmaan Fourier (FTIR) dan resonans magnet nuklear (NMR). Masa tindak balas, suhu tindak balas, jumlah mangkin dan nisbah mol EPO:IPA telah dipelbagaikan untuk menyiasat keupayaan IPA sebagai agen pembuka gelang. Didapati bahawa tindak balas pembukaan gelang berlaku dalam tempoh 6 jam setelah tindak balas berlangsung pada suhu 60°C dengan menggunakan 1 mL mangkin kompleks etanol boron triflorida dan nisbah EPO terhadap IPA adalah 1:3. Bagaimana pun, masih terdapat sisa gelang epoksida pada sampel polioliol yang dikesan oleh analisis FTIR dan NMR masing-masing pada $824\text{-}830\text{ cm}^{-1}$ dan 2.89 ppm. Analisis terperinci FTIR dan NMR mendapati bahawa IPA lebih cenderung untuk menyerang ikatan trigliserida ester berbanding gelang epoksida yang menghasilkan polioliol amida sebagai produk utama. Hasil kajian analisis spektroskopi jisim dan kromatografi penelapan gel menunjukkan bahawa polioliol amida menghasilkan polioliol rangkaian pendek dengan julat berat molekul polioliol pada 400-600 Da dengan taburan yang lebar. Selain daripada itu, polioliol amida mempunyai nilai kefungsiannya sebanyak 2, maka ianya sesuai digunakan sebagai bahan perantara untuk pelbagai tindak balas kimia. Lanjutan siasatan analisis termogravimetrik polioliol amida pula didapati mempunyai penguraian haba pada suhu 600°C , menunjukkan bahawa polioliol amida boleh digunakan sebagai bahan untuk tindak balas pada suhu yang tinggi.

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LIST OF ABBREVIATIONS

| | | |
|---------------------------|---|---|
| ^{13}C NMR | - | Carbon-13 Nuclear Magnetic Resonance |
| ^1H NMR | - | Proton Nuclear Magnetic Resonance |
| ASTM | - | American Standard Testing Method |
| $\text{BF}_3\text{-MeOH}$ | - | Boron trifluoride methanol complex |
| CDCl_3 | - | Deuterated chloroform |
| CHCA | - | α -cyano-4-hydroxynammic acid |
| Da | - | Dalton |
| DTGA | - | Derivative TGA |
| EPO | - | Epoxidized Palm Oil |
| ESO | - | Epoxidized soybean oil |
| f_n | - | Functionality |
| FTIR | - | Fourier Transform Infra-Red |
| GPC | - | Gel Permeation Chromatography |
| IPA | - | Isopropanolamine |
| MALDI-TOF | - | Matrix Assisted Laser Desorption Ionization –Time of Flight |
| M_n | - | Number average molecular weight |
| MPOB | - | Malaysia Palm Oil Board |
| MS | - | Mass spectrometry |
| M_v | - | Viscosity average molecular weight |
| MW | - | Molecular Weight |
| M_w | - | Weight average molecular weight |
| MWD | - | Molecular weight distribution |
| NMR | - | Nuclear Magnetic Resonance |
| OHV | - | Hydroxyl Value |

| | | |
|------------------|---|------------------------------------|
| OOC | - | Oxirane Oxygen Content |
| PDI | - | Polydispersity index |
| PO | - | Palm Oil |
| PO-p | - | Palm oil polyol |
| PU | - | Polyurethane |
| PVAC | - | Polyvinyl acetate |
| RBD | - | Refined Bleached Deodorized |
| S _N 1 | - | Unimolecular substitution reaction |
| S _N 2 | - | Bimolecular substitution reaction |
| t-BuOH | - | <i>tert</i> -butanol |
| TGA | - | Thermogravimetric Analysis |
| THF | - | Tetrahydrofuran |
| TMS | - | Tetramethylsilane |

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Polyols are compounds with multiple hydroxyl functionalities that are mainly used as reactants in various organic reactions. In polymer industry, polyols are used as starting materials for polyurethane (PU) production; by reacting with isocyanate through a stepwise polymerization. Wide varieties of polyols with low molecular weights (MW) such as glycerol and ethylene glycol and high MW such as polyether or polyester offer the versatility of the obtained polyurethanes (Zhang *et al.*, 2015). However, polyols are facing the same issues as other petroleum-derived materials i.e. depletion of petroleum sources, the uncertainty of world's market prices and environmental sustainability (Ionescu *et al.*, 2007). The awareness on producing the eco-friendly materials has triggered the extensive studies to develop polyols from renewable resources such as oils from plants or animals. These oils offer wide varieties of chemical transformation, readily available and relatively low price (Alam *et al.*, 2014; Lligadas *et al.*, 2010; Petrović *et al.*, 2008; Güner *et al.*, 2006; Sharma and Kundu, 2008; Ang *et al.*, 2014; Can *et al.*, 2006; Miao *et al.*, 2013; Zubir *et al.*, 2012). Plant oils such as soybean oil, canola oil, linseed oil, corn oil and jatropha oil have been successfully transformed into polyol precursors for PU reactions (Güner *et al.*, 2006; Belgacem and Gandini 2008; Ronda *et al.*, 2011; Espinosa and Meier, 2011). There are four common techniques in converting the plant oils into polyols; which are epoxidation/oxirane-ring opening, ozonolysis, hydroformylation, and transesterification/amidation (Hu *et al.*, 2014). Each technique produces the plant oil-

derived polyols with different structures and material properties (Belgacem and Gandini, 2008).

In Malaysia, the extensive developments to produce palm oil-based polyols have been progressively conducted by many researchers (Badri *et al.*, 2001; Tanaka *et al.*, 2008; Pawlik and Prociak, 2012; Velayutham *et al.*, 2009; Ang *et al.*, 2014; Prociak *et al.*, 2018). Like other plants oils, palm oil needs the addition of hydroxyl (OH) at its unsaturated site to obtain reactive polyols (Zhang *et al.*, 2007). Many methods have been introduced to modify triglycerides of the oil into polyols such as glycerolysis (Tanaka *et al.*, 2008), esterification/ transesterification (Mohammed *et al.*, 2013) and epoxidation (Hassan *et al.*, 2005; Pawlik and Prociak, 2012; Silverajah *et al.*, 2012; Ang *et al.*, 2014), transamidation of diethanolamine (Lee *et al.*, 2007) and enzymatic synthesis (McNeill and Berger, 1993). Among the routes, epoxidation of palm oil is well established and has great industrial importance with new studies and data are generated constantly (Bailosky *et al.*, 2013; Hazmi *et al.*, 2013; Dai *et al.*, 2009; Javni *et al.*, 2000). This is due to a better control of the oxidation process and the epoxy groups are inserted exactly at the position of double bonds to produce the epoxidized palm oil (EPO) (Caillol *et al.*, 2012). In return, the epoxidation route provides polyol with higher functionality and high molecular weight (Nohra *et al.*, 2013). The produced EPO can undergo ring opening reaction with hydroxyl-group bearer materials such as alcohol or acid to produce palm oil-polyol (PO-p) (Hazmi *et al.*, 2013; Sharma *et al.*, 2008). The epoxide ring-opening reaction is a widespread method for the functionalization of vegetable oils due to the existence of highly reactive three-member ring of the epoxy group that is prone to reaction with a range of nucleophile (Williams and Lawton, 2005).

In the ring opening reaction of epoxide group with the nucleophile, somehow catalyst was needed especially to activate the epoxide ring so that a weak nucleophile can attack the epoxide group (Ahn *et al.*, 2012). The most used homogenous catalysts is Lewis and Bronsted acids such as boron trifluoride, sodium stearate, stearic acid, sulfuric acid, p-toluenesulfonic acid or tetrafluoroboric (Caillol *et al.*, 2012; Ahn *et al.*, 2012).

Water, alcohol (glycerol and 1,2-propanediol), and acid (acetic acid, formic acid and phosphoric acid) (Miao *et al.*, 2013; Dahlke *et al.*, 1995) are among the reagents that have been used as ring opening reagent since this species bears atoms that can act as a nucleophile. However, self-oligomerization is most likely to occur when alcohol is used (Miao *et al.*, 2013) and mixture of mono, di-, and tri-ester compound are possible when acids are used as ring opening reagent. This makes the hydroxyl value of the polyols to be only half of the theoretical value (Miao *et al.*, 2013). Meanwhile, by using an amine as ring opening reagent, the reaction can be conducted at room temperature and produced high yield of products (Lifchits and Charette 2008; Biswas *et al.*, 2009). In addition, the amine reagent gives a high OH value to the obtained polyols (Dahlke *et al.*, 1995). The utilization of amine based reagent for ring opening of epoxidized plant oil has been done by previous researchers (Biswas *et al.*, 2005; Biswas *et al.*, 2009; Mohamed *et al.*, 2000). Biswas *et al.* (2005) had reacted diethylamine with epoxidized soybean oil under a mild reaction temperature without the use of any solvent. Meanwhile in 2009, they produced the same polyols using ionic liquid that gave a clean and environment friendly method with good yields of amide polyols. On the other hand, Mohamed *et al.* (2000) had used methylamine for ring opening of epoxidized soybean oil without any solvent but the reaction was conducted at temperature higher than 100°C. However, no details explanations on the mechanism of the ring opening reaction were discussed; for example how does the amine group attack the epoxide group during the reaction. Hence, the results presented in this study provide relevant information on how does nucleophile isopropanolamine (IPA) open the epoxide ring and what happened to the triglyceride linkage at the end of the reaction.

1.2 Problem Statement

Palm oil is one of the major products of Malaysia that is abundant available. Efforts have been made to discover the potential of palm oil as chemical precursors in industries; to replace the petroleum-based raw materials. One of the areas that look

promising is the production of polyol from palm oil from epoxidized palm oil (EPO). EPO can undergo the ring-opening reaction with alcohol to produce polyol palm oil. In chemistry point of view, it is important to understand the chemistry of the reaction as well as the factor that influence the progress of the reaction. Common reagents used for ring opening reaction of epoxidized plant oils are acids (e.g. fluoroboric acid and hydrochloric acid), alcohol (e.g. methanol and butanol) and water (Hazmi *et al.*, 2013; Sharma *et al.*, 2006). Acid-catalyzed ring opening reaction of epoxidized soybean oil (ESO) has been intensively studied by Ahn *et al.* (2012), Dai *et al.* (2009) and Liu and Erhan (2010). However, the ring opening using acids requires a complex multiple reaction steps and uses an excess solvent such as ammonia to neutralize the catalyst (Ni *et al.*, 2010; Garrison *et al.*, 2014)

A study conducted by Miao *et al.* (2013) on the production of ESO-based polyol using an isopropanolamine (IPA) as a ring opening reagent had shown a promising result where the polyol had higher hydroxyl value of 317 mg KOH/g. The reaction is quite simple where the ESO was mixed with IPA prior to react for 6 hours at temperatures of 80°C-100°C. Once completed, the reaction mixture was quenching with chloroform and the final product was recovered using liquid-liquid extraction. Meanwhile, the ratios of ESO to IPA were varied from 1.5:1 to 2.5:1. According to their works, the ring opening and the amidation reactions occurred simultaneously during the reaction. However, no details on mechanism were written in the paper. Therefore, this research has adopted the same approach by reacting IPA with EPO under some modifications.

From the chemistry point of view, IPA is a weak nucleophile and needs an acid-based co-catalyst to fasten the progress of the reaction (Ahn *et al.*, 2012). Lewis acid catalyst such as boron trifluoride (BF₃)-methanol complex catalyst was chosen as a co-catalyst from among strong acids such as hydrochloric (HCl) and sulfuric acids (H₂SO₄), since it is very stable and easy to handle (Morrison and Smith, 1964). In addition, a BF₃-methanol complex promotes a similar manner in reaction pathway like HCl and H₂SO₄ in which they gives no side reaction and no changes in the structure of the reactant as the reaction proceed (Morrison and Smith, 1964). Although there are many studies on the production of PO-p (Islam *et al.*, 2014; Ang

et al., 2014; Lumcharoen & Saravari 2014; Mohd Noor *et al.*, 2016; Zubir *et al.*, 2012; Arniza *et al.*, 2015), to date, there are no details on the mechanism of ring opening reaction on EPO with IPA/ BF₃-methanol complex. The discussions on previous studies were limited to the hydroxyl value of the polyols as an intermediate product for polyurethane application.

Acid catalyzed ring opening reaction of using epoxidized soybean oil (ESO) had been conducted by many researchers (Ahn *et al.*, 2012; Dai *et al.*, 2009; Liu and Erhan 2010). Like ESO, EPO had also underwent few series of experiments to convert it into polyol (Islam *et al.*, 2014; Ang *et al.*, 2014; Lumcharoen and Saravari, 2014; Mohd Noor *et al.*, 2016; Zubir *et al.*, 2012; Arniza *et al.*, 2015). However, there are no details explanations on the chemistry of ring opening reaction of EPO.

In this study, EPO underwent the ring-opening reaction with an amino alcohol in the presence of BF₃-methanol complex as a catalyst to produce palm oil polyol (PO-p). The studies were focused more on the mechanism of the ring opening reaction of EPO with IPA. In order to understand the mechanism of the reaction, the conditions of reaction like reaction time, reaction temperature, molar ratio and catalyst amount were varied.

1.3 Objectives

The main objective of this study is to develop an understanding of the reaction mechanism between EPO and IPA to produce palm oil polyol. The objective can be further subdivided as follows;

- i. To postulate the possible the mechanism of ring opening reaction between EPO and IPA at various reaction conditions such as reaction time, reaction temperature, EPO: IPA molar ratio and catalyst amount.
- ii. To characterize the properties of the palm oil polyol obtained in term of molecular structure, molecular weight, hydroxyl value and thermal analysis.

1.4 Scope of Study

In order to achieve the objective of this study, the works on synthesizing the palm oil polyol were conducted as follows;

- i. Various reaction times at fixed reaction temperature, EPO: IPA molar ratio and catalyst amount.
- ii. Various reaction temperatures at the fixed molar ratio, reaction time and catalyst amount.
- iii. Various molar ratio of IPA to EPO at fixed reaction temperature, reaction time and catalyst amount.
- iv. Various catalyst amount at fixed EPO:IPA molar ratio, reaction temperature and reaction time.

Upon completion, the final product was collected by removal of solvent using a rotary evaporator.

- a) Fourier transform infra-red (FTIR) and nuclear magnetic resonance (NMR) analyses were conducted to investigate ring opening mechanism between EPO and IPA.
- b) Mass spectroscopy (MS) and gel permeation chromatography (GPC) analyses were conducted to determine the molecular weight and the structure polyol.
- c) The hydroxyl value analysis (OHV) was carried out to calculate the OH number.
- d) Thermogravimetric analysis (TGA) was conducted to analyse thermal stability of polyol.

REFERENCES

- Ahn, B.J.K., Kraft, S. and Sun, X.S. (2012). Solvent-Free Acid-Catalyzed Ring-Opening of Epoxidized Oleochemicals using Stearates/Stearic Acid, and its Applications. *Journal of Agricultural and Food Chemistry*, 60, 2179–2189.
- Al-Saad, K.A., Vladimir, Z., William F. S., Knowles, N.R., Richard, M. H. and Herbert H. J. (2003). Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry of Lipids: Ionization and Prompt Fragmentation Patterns. *Rapid Communications in Mass Spectrometry*. 17(1),87–96.
- Alam, M., Sharmin E., Ashraf, S.M and Ahmad, S. (2004). Newly Developed Urethane Modified Polyetheramide-Based Anticorrosive Coatings from A Sustainable Resource. *Progress in Organic Coatings*, 50(4), 224–230.
- Alam, M., Akram, D., Sharmin, E., Zafar, F. and Ahmad, S. (2014). Vegetable Oil Based Eco-Friendly Coating Materials: A Review Article. *Arabian Journal of Chemistry*, 7(4), 469–479.
- Alam, M. and Alandis, N. (2011). Development of Ambient Cured Polyesteramide Coatings from Linseed Oil: a Sustainable Resource. *Journal of Polymers and the Environment*, 19(2), 391–397.
- Alferd, M. and Hermann, K. (1989). *U. S. Patent No 4886893A*. Retrieved on December 10, 2017 from <https://patents.google.com>
- Ali, E.S., Zubir, S.A. and Ahmad, S. (2012). Clay Reinforced Hyperbranched Polyurethane Nanocomposites Based on Palm Oil Polyol as Shape Memory Materials. *Advanced Materials Research*, 548,115–118.
- Ang, K.P., Lee, C.S., Cheng, S.F. and Cheng Hock, C. (2014). Polyurethane Wood Adhesive from Palm Oil-Based Polyester Polyol. *Journal of Adhesion Science and Technology*, 28(11), 1020–1033.

- Ang, K.P., Lee, C.S., Cheng, S.F. and Chuah, C.H. (2014). Synthesis Of Palm Oil-Based Polyester Polyol for Polyurethane Adhesive Production. *Journal of Applied Polymer Science*, 131(6), 39967.
- Arniza, M.Z., Hoong, S.S., Idris, Z., Yeong, S.K., Hazimah, A.H., Ahmad, K.D., and Choo, Y. M. (2015). Synthesis of Transesterified Palm Olein-Based Polyol and Rigid Polyurethanes from this Polyol. *Journal of the American Oil Chemists' Society*, 92(2), 243–255.
- Ayorinde, F.O., Elhilo, E. and Hlongwane, C. (1999). Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight Mass Spectrometry of Canola, Castor and Olive Oils. *Rapid Communications in Mass Spectrometry*, 13(8),737–739.
- Badri, K.H., Ahmad, S.H. and Zakaria, S. (2001). Production of A High-Functionality RBD Palm Kernel Oil-Based Polyester Polyol. *Journal of Applied Polymer Science*, 81(2), 384–389.
- Badri, K.H., Othman, Z. and Ahmad, S.H. (2004). Rigid Polyurethane Foams from Oil Palm Resources. *Journal of Materials Science*, 39(16–17),5541–5542.
- Bailosky, L.C., Bender, L.M., Daniel, B., Riaz, A. C., Gary, P.C., Kenneth, J. G., Candice, R. M., Jude, T.R., Guy, J. S. and David, J. T. (2013). Synthesis Of Polyether Polyols With Epoxidized Soy Bean Oil. *Progress in Organic Coatings*, 76(12),1712–1719.
- Belgacem, M.N. and Gandini, A. (2008). *Chapter 3 - Materials from Vegetable Oils: Major Sources, Properties and Applications*. In M. N. Belgacem and A. Gandini (Ed). *Monomers, Polymers and Composites from Renewable Resources*. (39–66). Amsterdam: Elsevier.
- Biswas, A., Sharma, B. K., Doll, K. M., Erhan, S. Z., Willett, J. L. and Cheng, H. N. (2009). Synthesis of an Amine–Oleate Derivative Using an Ionic Liquid Catalyst. *Journal of Agricultural and Food Chemistry*. 57(18),8136–8141.
- Biswas, A., Adhvaryu, A., Gordon, S. H., Erhan, S. Z. and Willett, J. L. (2005). Synthesis of Diethylamine-Functionalized Soybean Oil. *Journal of Agricultural and Food Chemistry*. 53(24),9485–90.
- Borriello, A., Nicolais, L. and Huang, S.J., (2005). Poly(Amide-Ester) Derived from Dicarboxylic Acid and Aminoalcohol. *Journal of Applied Polymer Science*, 95(2), 362–368.

- Caillol, S., Desroches, M., Boutevin, G., Loubat, C., Auvergne, R. and Boutevin, B. (2012). Synthesis of New Polyester Polyols from Epoxidized Vegetable Oils and Biobased Acids. *European Journal of Lipid Science and Technology*, 114(12).
- Calvano, C.D., Palmisano, F. and Zambonin, C.G., (2005). Laser Desorption/Ionization Time-Of-Flight Mass Spectrometry of Triacylglycerols in Oils. *Rapid Communications in Mass Spectrometry: RCM*. 19(10),1315–1320.
- Campanella, A. and Baltanás, M.A. (2005a). Degradation of The Oxirane Ring of Epoxidized Vegetable Oils In Liquid-Liquid Systems: I. Hydrolysis and Attack By H₂O₂. *Latin American Applied Research*, 35(3),205–210.
- Campanella, A. and Baltanás, M.A. (2005b). Degradation of The Oxirane Ring of Epoxidized Vegetable Oils In Liquid-Liquid Systems: II. Reactivity With Solvated Acetic and Peracetic Acids. *Latin American Applied Research*. 35(3), 211–216.
- Can, E., Wool, R.P. and Küseföglü, S. (2006). Soybean- and Castor-Oil-Based Thermosetting Polymers: Mechanical Properties. *Journal of Applied Polymer Science*. 102,1497–1504.
- Chang, C.W. and Lu, K.T. (2012). Natural Castor Oil Based 2-Package Waterborne Polyurethane Wood Coatings. *Progress in Organic Coatings*. 75(4),435–443.
- Chaudhari, A., Gite, V., Rajput, S., Mahulikar, P. and Kulkarni, R. (2013). Development of Eco-Friendly Polyurethane Coatings Based On Neem Oil Polyetheramide. *Industrial Crops and Products*. 50(0), 550–556.
- Chaudhari, A.B., Tatiya, P. D., Hedao, R. K., Kulkarni, R. D. and Gite, V. V. (2013). Polyurethane Prepared from Neem Oil Polyesteramides for Self-Healing Anticorrosive Coatings. *Industrial & Engineering Chemistry Research*. 52(30), 10189–10197.
- Chaudhari, A.B., Anand, A., Rajput, S.D., Kulkarni, R.D. and Gite, V.V. (2013). Synthesis, Characterization and Application of Azadirachta Indica Juss (Neem Oil) Fatty Amides (AIJFA) Based Polyurethanes Coatings: A Renewable Novel Approach. *Progress in Organic Coatings*. 76(12),1779–1785.
- Chen, R., Zhang, C. and Kessler, M.R. (2014). Polyols and Polyurethanes Prepared from Epoxidized Soybean Oil Ring-Opened by Polyhydroxy Fatty Acids with Varying OH Numbers. *Journal of Applied Polymer Science*. 41213, 1-10

- Chini, M., Crotti, P., Gardelli, C. and Macchia, F. (1992). Metal Salt-Promoted Alcoholysis of 1,2-Epoxides. *Synlett*. 1992(8),673–676.
- Chuayjuljit, S., Maungchareon, A. and Saravari, O. (2010). Preparation and Properties of Palm Oil-Based Rigid Polyurethane Nanocomposite Foams. *Journal of Reinforced Plastics and Composites*. 29(2), 218–225.
- Clayden, J., Greeves, N. & Warren, S. (2012). *Organic Chemistry* (2nd ed.), New York: Oxford University Press.
- Coud, V. V., Pradhan, N.C. and Patwardhan, A. V. (2006). Epoxidation of Karanja (Pongamia Glabra) Oil by H₂O₂. *Journal of the American Oil Chemists' Society*. 83(7), 635–640.
- Dahlke, B., Hellbardt, S., Paetow, M. and Zech, W.H. (1995). Polyhydroxy Fatty Acids and their Derivatives from Plant Oils. *Journal of the American Oil Chemists' Society*. 72(3), 349–353.
- Dai, H., Yang, L., Lin, B., Wang, C. and Shi, G. (2009). Synthesis and Characterization of the Different Soy-Based Polyols by Ring Opening of Epoxidized Soybean Oil with Methanol, 1,2-Ethandiol and 1,2-Propanediol. *Journal of the American Oil Chemists' Society*. 86(3), 261–267.
- Deffense, E.(1985). Fractionation of Palm Oil. *Journal of the American Oil Chemists' Society*. 62(2), 376–385.
- Derawi, D. and Salimon, J. (2010). Optimization on Epoxidation of Palm Olein by Using Performic Acid. *E-Journal of Chemistry*.7(4),1440–1448.
- Dinda, S., Patwardhan, A. v., Goud, V. V., and Pradhan, N. C. (2008). Epoxidation of Cottonseed Oil by Aqueous Hydrogen Peroxide Catalysed by Liquid Inorganic Acids. *Bioresource Technology*,. 99(9), 3737–3744.
- Dotan, A., (2014). Biobased Thermoset. In Sydney H. G and Hanna D. K (Ed) *Handbook of Thermoset Plastics : 3rd Ed* (577- 622) USA: Elsevier
- Dumont, M.J., Kharraz, E. and Qi, H. (2013). Production of Polyols and Mono-ols from 10 North-American Vegetable Oils by Ozonolysis and Hydrogenation: A Characterization Study. *Industrial Crops and Products*. 49(0),830–836..
- Erhan, S.Z. and Bagby, M.O. (1994). Polymerization of Vegetable Oils and Their Uses in Printing Inks. *Journal of the American Oil Chemists' Society*. 71(11),1223–1226.

- Farias, M., Martinelli, M. and Bottega, D.P. (2010). Epoxidation of Soybean Oil Using A Homogeneous Catalytic System Based on A Molybdenum (VI) Complex. *Applied Catalysis A: General*. 384(1–2), 213–219.
- FOASTAT, 2014. *Food and Agriculture Organization of The United Nations*.
- Frisch Jr, K.C. (2002). Chapter 16 - Chemistry and technology of polyurethane adhesives. In M. Chaudhury and A. V Pocius, (Ed). *Adhesion Science and Engineering*. Amsterdam: Elsevier Science B.V.(759–812).
- Gan, L.H., Goh, S.H. and Ooi, K.S. (1992). Kinetic Studies of Epoxidation and Oxirane Cleavage of Palm Olein Methyl Esters. *Journal of the American Oil Chemists' Society*. 69(4), 347–351.
- Garrison, T.F., Kessler, M.R. and Larock, R.C. (2014). Effects of Unsaturation and Different Ring-Opening Methods on The Properties of Vegetable Oil-Based Polyurethane Coatings. *Polymer*. 55(4), 1004–1011.
- Gidden, J., Liyanage, R., Durham, B. and Jackson O. L. (2007). Reducing Fragmentation Observed in The Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight Mass Spectrometric Analysis of Triacylglycerols in Vegetable Oils. *Rapid Communications in Mass Spectrometry : RCM*. 21,1951–1957.
- Goud, V. V., Patwardhan, A. V., Dinda, S. and Pradhan, N.C. (2007). Epoxidation of Karanja (*Pongamia Glabra*) Oil Catalysed By Acidic Ion Exchange Resin. *European Journal of Lipid Science and Technology*. 109(6), 575–584.
- Goud, V. V., Patwardhan, A. V. and Pradhan, N.C. (2006). Studies on The Epoxidation of Mahua Oil (*Madhumica Indica*) by Hydrogen Peroxide. *Bioresource Technology*. 97(12),1365–1371.
- Gunstone, F. (1993). The Study of Natural Epoxy Oils and Epoxidized Vegetable Oils by ¹³C Nuclear Magnetic Resonance Spectroscopy. *Journal of the American Oil Chemists Society*. 70(11), 1139–1144.
- Guo, A., Cho, Y. and Petrović, Z.S. (2000). Structure and Properties of Halogenated and Nonhalogenated Soy-Based Polyols. *Journal of Polymer Science Part A: Polymer Chemistry*. 38(21), 3900–3910.
- Guo, A., Zhang, W. and Petrovic, Z.S. (2006). Structure–Property Relationships in Polyurethanes Derived from Soybean Oil. *Journal of Materials Science*. 41(15), 4914–4920.

- Guo, Y., Hardesty, J. H., Mannari, V. M. and Massingill Jr, J. L. (2007). Hydrolysis of Epoxidized Soybean Oil in The Presence Of Phosphoric Acid. *Journal of the American Oil Chemists' Society*. 84(10), 929–935.
- Hassan, H.A., Hoong, S.S. and Norhisam, M. (2005). Palm- Based Polyol for Coating. *MPOB Information Series*.
- Hazmi, A.S.A., Aung, M. M., Abdullah, L. C., Salleh, M.Z. and Mahmood, M. H. (2013). Producing Jatropha Oil-Based Polyol Via Epoxidation and Ring Opening. *Industrial Crops and Products*. 50(0), 563–567.
- He, W., Fang, Z., Ji, D., Chen, K., Wan, Z., Gan, H., Li, X., Tang, S., Zhang, K. and Guo, K. (2013). Epoxidation of Soybean Oil by Continuous Micro-Flow System with Continuous Separation. *Organic Process Research and Development*. 17(9), 1137–1141.
- Holser, R.A. (2008). Transesterification of Epoxidized Soybean Oil to Prepare Epoxy Methyl Esters. *Industrial Crops and Products*. 27(1),130–132.
- Hu, S., Luo, X. and Li, Y. (2014). Polyols and Polyurethanes from the Liquefaction of Lignocellulosic Biomass. *ChemSusChem*. 7(1), 66–72.
- Ifa, L., Nurdjannah, Aladin, A., Sabara, Z. and Jusoff, K. (2013). Identification of Urethane Linkage, Soft Segment Polyol and Hard Segment Polyurea in Polyurethane from Palm Oil Based Polyol. *World Applied Sciences Journal*. 26,50–54.
- Ionescu, M (2005). Polyols From Renewable Resources - Oleochemical Polyols. In *Chemistry and Technology of Polyols for Polyurethanes*. Shropshire, UK: Rapra technology. (435–475).
- Ionescu, M., Petrović, Z. and Wan, X. (2007). Ethoxylated Soybean Polyols for Polyurethanes. *Journal of Polymers and the Environment*. 15(4),237–243.
- Islam, M.R., Beg, M.D.H. and Jamari, S.S. (2014). Development of Vegetable-Oil-Based Polymers. *Journal of Applied Polymer Science*, 131(18), 40787(1 of 13)
- Jackson O Lay, J. (2012). Characterization of lipid by MALDI mass spectrometry. *AOCS Lipid Library*.
- Javni, I., Petrovic, Z.S., Guo, A. and Fuller, R. (2000). Thermal Stability of Polyurethanes Based on Vegetable Oils. *Journal of Applied Polymer Science*. 77(8),1723–1734.

- Jenkins, R.C. (2005).WO1992011097A1. Retrieved on April 4, 2017, from <https://patents.google.com/patent/WO1992011097A1>
- Jiang, J., (2012). Epoxidation of Soybean Oil Catalyzed by Peroxo Phosphotungstic Acid Supported on Modified Halloysite Nanotubes. *Applied Surface Science*. 258(17), 6637–6642.
- Khoe, T.H. and Frankel, E.N. (1976). Rigid Polyurethane Foams from Diethanolamides of Carboxylated Oils and Fatty Acids. *Journal of the American Oil Chemists Society*. 53(1), pp.17–19.
- Khot, S.N., Lascala, J. J., Can, E., Morye, S. S., Williams, G. I., Palmese, G. R., Kusefoglul, S. H. and Wool, R. P. (2001). Development and Application of Triglyceride-Based Polymers and Composites. *Journal of Applied Polymer Science*. 82,703–723.
- Kim, J.R. and Sharma, S. (2012). The Development and Comparison of Bio-thermoset Plastics from Epoxidized Plant Oils. *Industrial Crops and Products*. 36(1),485–499.
- Kollbe Ahn, B., Wang, H., Robinson, S., Shrestha, T. B., Troyer, D. L., Bossmann, S. H. and Sun, X. S. (2012). Ring Opening of Epoxidized Methyl Oleate using A Novel Acid-functionalized Iron Nanoparticle Catalyst. *Green Chemistry*. 14, 136.
- Kong, X., Liu, G. and Curtis, J.M. (2011). Characterization of Canola Oil Based Polyurethane Wood Adhesives. *International Journal of Adhesion and Adhesives*. 31(6),559–564.
- L. H. Sperling (2006). *Introduction to Physical Polymer Science*,(4th ed). USA: Wiley
- Lampman, G.M., Pavia, D. L., Kriz, G. S. and Vyvyan, J. R. (2010). *Introduction to Spectroscopy*, (4th ed). USA;Brooks/Cole.
- Lee, C.S., Ooi, T. L., Chuah, C. H. and Ahmad, S.(2007). Rigid Polyurethane Foam Production from Palm Oil-Based Epoxidized Diethanolamides. *Journal of the American Oil Chemists' Society*. 84(12), 1161–1167.
- Lee, G.C., Wang, D. L., Hp. Y. F. and Shaw, J. F. (2004). Lipase-Catalyzed Alcoholysis of Triglycerides for Short-Chain Monoglyceride Production. *Journal of the American Oil Chemists' Society*. 81(6), 533–536.

- Li, Y.Y., Luo, X. and Hu, S. (2015). Bio-based Polyols and Polyurethanes. *Bio-based Polyols and Polyurethanes*. 1–79.
- Lifchits, O. and Charette, A.B. (2008). A Mild Procedure for the Lewis Acid-Catalyzed Ring-Opening of Activated Cyclopropanes with Amine nucleophiles. *Organic Letters*. 10(13), 2809–2812.
- Liu, Z. and Erhan, S.Z. (2010). Ring-opening Polymerization of Epoxidized Soybean Oil. *Journal of the American Oil Chemists' Society*. 87(4), 437–444.
- Lligadas, G., Ronda, J.C., Galia, M. and Cadiz, V. (2010). Oleic and Undecylenic Acids as Renewable Feedstocks in the Synthesis of Polyols and Polyurethanes. *Polymers*. 2, 440–453.
- Lligadas, G., Ronda, J.C., Galia, M. and Cadiz, V. (2010). Plant Oils as Platform Chemicals for Polyurethane Synthesis: Current State-of-the-Art. *Biomacromolecules*. 11(11). 2825–2835.
- Low, J.H., Rahman, W.A.W.A. and Jamaluddin, J. (2015). Structural Elucidation of Tannins of Spent Coffee Grounds by CP-MAS ¹³C NMR and MALDI-TOF MS. *Industrial Crops and Products*. 69, 456–461.
- Lu, Y. and Larock, R.C. (2008). Soybean-Oil-Based Waterborne Polyurethane Dispersions: Effects of Polyol Functionality and Hard Segment Content on Properties. *Biomacromolecules*. 9(11), 3332–3340.
- Lumcharoen, D. and Saravari, O. (2014). Preparation and Characterization of Flexible Polyurethane Foams from Palm Oil-Based Polyol. *Advanced Materials Research*. 911, 352–356.
- Mahapatra, S.S. and Karak, N. (2004). Synthesis and Characterization of Polyesteramide Resins From Nahar Seed Oil For Surface Coating Applications. *Progress in Organic Coatings*. 51(2), 103–108.
- Marcovich, N.E., Kuranska, M., Prociak, A., Malewska, E. and Kulpa, K. (2017). Open Cell Semi-Rigid Polyurethane Foams Synthesized Using Palm Oil-Based Bio-Polyol. *Industrial Crops and Products*. 102, 88–96
- McNeill, G.P. and Berger, R.G. (1993). Enzymatic Glycerolysis of Palm Oil Fractions and A Palm Oil Based Model Mixture: Relationship Between Fatty Acid Composition and Monoglyceride Yield. *Food Biotechnology*. 7(1), 75–87.

- Meshram, P. D., Puri, R. G., Patil, A. L. and Gite, V. V. (2013). Synthesis and Characterization of Modified Cottonseed Oil Based Polyesteramide for Coating Applications. *Progress in Organic Coatings*. 76(9), 1144–1150.
- Miao, S., Zhang, S., Su, Z. and Wang, P. (2013). Synthesis of Bio-Based Polyurethanes from Epoxidized Soybean Oil and Isopropanolamine. *Journal of Applied Polymer Science*. 127,1929–1936.
- Miao, S., Wang, P., Su, Z. and Zhang, S. (2013). Vegetable-Oil-Based Polymers as Future Polymeric Biomaterials. *Acta Biomaterialia*. 10(4), 1692-1704.
- Michael, S. (2012). Health and Safety. In *Szycher's Handbook of Polyurethanes, Second Edition*. CRC Press, (449–494).
- Mihail Ionescu (2005). *Chemistry and Technology of Polyols for Polyurethanes*, Shropshire, UK: Rapra Technology Limited.
- Mohamed, H.A., Badran, B. M., Rabie, A. M. and Morsi, S. M. M. (2014). Synthesis and Characterization of Aqueous (Polyurethane/Aromatic Polyamide Sulfone) Copolymer Dispersions from Castor Oil. *Progress in Organic Coatings*. 77(5), 965–974.
- Mohamed, H. A., Badran, B.M. and Aglan, H. A. (2000). Waterborne Methylamine Adduct as Corrosion Inhibitor for Surface Coatings. *Journal of Applied Polymer Science*. 80,286–296.
- Mohammed, I.A., Al-Mulla, E.A.J., Abdul Kadar, N. K. and Ibrahim, M. (2013). Structure-Property Studies of Thermoplastic and Thermosetting Polyurethanes Using Palm and Soya Oils-Based Polyols. *Journal of Oleo Science*. 62,1059–72.
- Mohd Noor, M.A., Sendjarevic, V., Hoong, S. S., Sendjarevic, I., Tuan Ismail, T. N. M., Hanzah, N.A., Mohd Noor, N., Kosheela D.P.P. Ghazali, R. and Hassan, H. A. (2016). Molecular Weight Determination of Palm Olein Polyols by Gel Permeation Chromatography Using Polyether Polyols Calibration. *Journal of the American Oil Chemists' Society*. 93(5),721–730.
- Mohd Noor, N., Tuan Ismail, T. N. M., Kian, Y. S. and Hassan, H. A. (2013). Synthesis of Palm-Based polyols: Effect of K10 Montmorillonite Catalyst. *Journal of Oil Palm Research*, 25(1),92–99.
- Montero de Espinosa, L. and Meier, M.A.R. (2011). Plant oils: The perfect Renewable Resource for Polymer Science?! *European Polymer Journal*. 47(5),837–852.

- Morrison, W.R. and Smith, L.M. (1964). Preparation of Fatty Acid Methyl Esters and Dimethyl Acetals from Lipids with Boron Trifluoride Methanol. *Journal of Lipid Research*, 5(13), 600–608.
- Ni, B., Yang, L., Wang, C., Wang, L. and Finlow, D. E. (2010). Synthesis and Thermal Properties of Soybean Oil-Based Waterborne Polyurethane Coatings. *Journal of Thermal Analysis and Calorimetry*, 100, 239–246.
- Ning, L. and Newbold, T. (2008). W02008130646A1. Retrieved on 25 Oct, 2017 from <https://patents.google.com/patent/WO2008130646A1>.
- Nohra, B., Candy, L., Blanco, J.F., Guerin, C., Raoul, Y. and Mouloungui, Z. (2013). From Petrochemical Polyurethanes to Biobased Polyhydroxyurethanes. *Macromolecules*, 46(10), 3771–3792.
- Ollevier, T. and Lavie-Compin, G. (2004). Bismuth Triflate-Catalyzed Mild and efficient Epoxide Opening by Aromatic Amines Under Aqueous Conditions. *Tetrahedron Letters*, 45(1), 49–52.
- Pawlik, H. and Prociak, A. (2012). Influence of Palm Oil-Based Polyol on the Properties of Flexible Polyurethane Foams. *Journal of Polymers and the Environment*, 20, 438–445.
- Petrovic, Z. (2008). Polyurethanes from Vegetable Oils. *Polymer Reviews*, 48(1), 109–155.
- Petrović, Z. and Yang, L. (2007). Network Structure and Properties of Polyurethanes from Soybean Oil. *Journal of Applied Polymer Science*, 105(5), 2717–2727.
- Petrović, Z.S., Zlatanic, A., Lava, C. C. and Snezana, S. F. (2002). Epoxidation of Soybean Oil in Toluene with Peroxoacetic and Peroxoformic Acids - Kinetics and Side Reactions. *European Journal of Lipid Science and Technology*, 104(5), 293–299.
- Petrović, Z.S., Cvetkovic, I., Hong, D. P., Wan, X., Zhang, W., Abraham, T. and Malsam, J. (2008). Polyester Polyols and Polyurethanes from Ricinoleic Acid. *Journal of Applied Polymer Science*, 108(2), 1184–1190.
- Petrović, Z.S. (2010). Polymers From Biological Oils. *Contemporary Materials*, 1(1), 39–50.
- Petrović, Z.S. (2008). Polyurethanes from Vegetable Oils. *Polymer Reviews*, 48(1), 109–155.

- Prestat, G., Baylon, C., Heck, M. P. and Mioskowski, C. (2000). Lewis Acid-Catalyzed Regiospecific Opening of Vinyl Epoxides by Alcohols. *Tetrahedron Letters*, 41(20), 3829–3831.
- Prociak, A., Malewska, E., Kuranska, M., Bak, S. and Budny, P. (2018). Flexible Polyurethane Foams Synthesized With Palm Oil-Based Bio-Polyols Obtained With The Use of Different Oxirane Ring Opener. *Industrial Crops and Products*, 115, 69–77.
- Rios, L. A., Echeverri, D. A. and Franco, A. (2011). Epoxidation of Jatropha Oil Using Heterogeneous Catalysts Suitable For The Prileschajew Reaction: Acidic Resins and Immobilized Lipase. *Applied Catalysis A: General*, 394(1–2), 132–137.
- Ronda, J.C., Lligadas, G., Galia, M. and Cadiz, V. (2011). Vegetable Oils as Platform Chemicals for Polymer Synthesis. *European Journal of Lipid Science and Technology*, 113(1), 46–58.
- Rüsch Gen. Klaas, M. and Warwel, S. (1999). Complete and Partial Epoxidation of Plant Oils by Lipase-Catalyzed Perhydrolysis. *Industrial Crops and Products*, 9(2), 125–132.
- Saenz, P., Cachau, R. E., Seoane, G., Kieninger, M. and Ventura, O. N. (2006). A New Perspective in the Lewis Acid catalyzed Ring Opening of Epoxides. Theoretical Study of Some Complexes Of Methanol, Acetic Acid, Dimethyl Ether, Diethyl Ether, and Ethylene Oxide with Boron Trifluoride. *Journal of Physical Chemistry A*, 110(41), 11734–11751.
- Saenz, P. M., Cachau, R. E., Seoane, G. and Ventura, O. N. (2009). Regioselective Epoxide Ring-Opening Using Boron Trifluoride Diethyl Etherate: DFT Study of An Alternative Mechanism to Explain The Formation of Syn-Fluorohydrins. *Journal of Molecular Structure: THEOCHEM*, 904(1–3), 21–27.
- Salimon, J., Abdullah, B. M., Yusop, R. M., Salih, N. and Yousif, E. (2013). Synthesis and Optimization Ring Opening of Monoepoxide Linoleic Acid Using p-Toluenesulfonic Acid. *SpringerPlus*, 2(1), 429.
- Schuchardt, U., Sercheli, R. and Vargas, R.M. (1998). Transesterification of Vegetable Oils: A review. *Journal of the Brazilian Chemical Society*, 9(3), 199–210.

- Seniha Güner, F., Yağcı, Y. and Tuncer Erciyes, A. (2006). Polymers from Triglyceride Oils. *Progress in Polymer Science*, 31(7), 633–670.
- Sharma, B. K., Adhvaryu, A, Liu, Z. and Erhan, S. Z. (2006). Chemical Modification of Vegetable Oils for Lubricant Applications. *Journal of the American Oil Chemists' Society*, 83(2), 129–136.
- Sharma, B.K., Liu, Z., Adhvaryu, A. and Erhan, S. Z. (2008). One-Pot Synthesis of Chemically Modified Vegetable Oils. *Journal of Agricultural and Food Chemistry*, 56(9), 3049–3056.
- Sharma, V. and Kundu, P.P. (2008). Condensation Polymers from Natural Oils. *Progress in Polymer Science*, 33(12), 1199–1215.
- Silverajah, V.S.G., Ibrahim, N. A., Zainuddin, N., Wan Yunus, W. M. Z. and Abu Hassan, H. (2012). Mechanical, Thermal and Morphological Properties of Poly(Lactic Acid)/Epoxidized Palm Olein Blend. *Molecules (Basel, Switzerland)*, 17(10), 11729–47.
- Smith, J.G.(2006). *Organic Chemistry* (International Ed). New York: Mc Graw Hill.
- Suresh, K.I. and Kishanprasad, V.S.(2005). Synthesis, Structure, and Properties of Novel Polyols from Cardanol and developed Polyurethanes. *Industrial and Engineering Chemistry Research*, 44(13), 4504–4512.
- Tanaka, R., Hirose, S. and Hatakeyama, H. (2008). Preparation and Characterization of Polyurethane Foams using a Palm Oil-based Polyol. *Bioresource Technology*, 99, 3810–3816.
- de Vasconcelos Vieira Lopes, R., Loureiro, N. P. D., Pezzin, A. P. T., Gomez, A. C. M., Rescl, I. S. and Sales, M. J. A. (2013). Synthesis of Polyols and Polyurethanes from Vegetable Oils–Kinetic and Characterization. *Journal of Polymer Research*, 20(9), 238.
- Velayutham, T.S., Abd Majid, W. H., Ahmad, A. B., Kang, G. Y. and Gan, S. N. (2009). Synthesis and Characterization of Polyurethane Coatings derived from Polyols Synthesized with Glycerol, Phthalic Anhydride and Oleic Acid. *Progress in Organic Coatings*, 66(4), 367–371.
- Wan Rosli, W.D., Kumar, R. N., Mek Zah, S. and Mohd Hilmi, M. (2003). UV Radiation Curing of Epoxidized Palm Oil-Cycloaliphatic Diepoxide System Induced by Cationic Photoinitiators for Surface Coatings. *European Polymer Journal*, 39, 593–600.

- Wang, Z., Zhang, X., Wang, R., Kang, H., Qiao, B., Ma, J., Zhang, L. and Wang, H. (2012). Synthesis and Characterization of Novel Soybean-Oil-Based Elastomers with Favorable Processability and Tunable Properties. *Macromolecules*, 45(22), 9010–9019.
- Wicks, Z. W., Jones, F. N., Pappas, S. P. and Wicks, D. A. (1979). *Organic Coatings: Science and Technology* (3rd ed). USA:Wiley
- Williams, D.B.G. and Lawton, M. (2005). Aluminium Triflate: A Remarkable Lewis Acid Catalyst for The Ring Opening of Epoxides by Alcohols. *Organic & biomolecular chemistry*, 3, 3269–3272.
- Woodcock, D. (2012). *Plant Oil Derived Monomers for Use in Materials*. PhD Thesis. University of Warwick.
- Wrasidlo, W. (1974). *Thermal analysis of polymers*. In Mark, H. F. (Ed) *Encyclopedia of Polymer Science and Technology*, 4th Ed. USA:Wiley
- Yunus, R., Lye, O. T., Razi, A. F. and Basri, S. (2002). A Simple Capillary Column GC Method for Analysis of Palm Oil-Based Polyol Esters. *Journal of the American Oil Chemists' Society*, 79,1075–1080.
- Zain, N.M., Hj Ahmad, S., Ali, E. S., Zubir, S. A. and Ahad, N. A. (2012). Characteristics of Hydrolysis Resistant Polycaprolactone/Palm Kernel Oil Based Polyol. *Advanced Materials Research*, 576, 334–337.
- Zhang, J., Tang, J.J. and Zhang, J.X. (2015). Polyols Prepared from Ring-Opening Epoxidized Soybean Oil by a Castor Oil-Based Fatty Diol. *Hindawi - International Journal of Polymer Science*, 2015, 529235.
- Zhang, L., Jeon, H. K., Malsam, J., Herrington, R. and Maccosko, C. W. (2007). Substituting Soybean Oil-Based Polyol into Polyurethane Flexible Foams. *Polymer*, 48(22), 6656–6667.
- Zieleniewska, M., Auguscik, M., Prociak, A. and Rojek, P. (2014). Polyurethane-Urea Substrates from Rapeseed Oil-Based Polyol for Bone Tissue Cultures Intended for Application in Tissue Engineering. *Polymer Degradation and Stability*, 108, 241-249.
- Zubir, S.A., Ali, E. S., Hj Ahmad, S., Zain, N. M. and Wai, S. K. (2012). Polyurethane/Clay Shape Memory Nanocomposites Based on Palm Oil Polyol. *Advanced Materials Research*, 576, 236–239.