RENEWABLE RESOURCES POLYOL AS CHAIN EXTENDERS FOR WATERBORNE POLYURETHANE DISPERSION

KHAIRUL AZHAR BIN ABDUL HALIM

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Polymer)

Faculty of Chemical Engineering
Universiti Teknologi Malaysia

SEPTEMBER 2013

RENEWABLE RESOURCES POLYOL AS CHAIN EXTENDERS FOR WATERBORNE POLYURETHANE DISPERSION

KHAIRUL AZHAR BIN ABDUL HALIM

UNIVERSITI TEKNOLOGI MALAYSIA

To my beloved mother and father.

ACKNOWLEDGEMENT

In the name of the Almighty Allah, the most gracious and merciful praised be to God. With the deepest gratitude I wish to thank every person who has come into my life and inspired me through their presence. For generously sharing her wisdom, support and encouragement, I would like to thank my supervisor Dr. Rohah A. Majid, without her I would have not been able to complete this writing. I would also like to express my gratitude toward my friends and family who has helped me through their love and moral support. Lastly I would like to thank the supporting staff of Universiti Teknologi Malaysia with their kindness and contributions.

ABSTRACT

Waterborne polyurethane dispersion (PUD) was synthesized by using inverse dispersion prepolymer technique. A prepolymer mixture of isophorone diisocyanate and polypropylene glycol was extended with five types of chain extenders. The first two types are from the amine based chain extenders which are ethylene diamine and hydrazine; the other three are diol based chain extenders, one from a petroleum based diol which is ethylene glycol and the other two from renewable resources which are castor oil (CO) and palm oil based-polyols (POP). In attempt to reduce the toxicity by replacing the toxic amine based chain extender with diols. Furthermore, renewable resources chain extenders were used to decrease dependency on petroleum which is an expensive and depletable resources. Fourier Transform Infrared Spectroscopy analysis showed that all samples have been successfully synthesized into PUDs, based on the absorption peaks at 1537-1539 cm^{-1} and 1718-1725 cm^{-1} which corresponded to the NH and carbonyl peaks of urethane respectively and also the absence of -NCO peak at 2275 cm^{-1}. Palm oil-based PUD has the highest viscosity of 5.4 cP, particle size of 1.738 micron but low solid content of 31 wt%. The oil based chain extended polyurethane exhibited better thermal stability than the rest of the samples. This is assumed due to the hydroxyl group of the triglycerides which may react with isocyanate at high temperature to produce crosslink polyurethane. However, the oil based chain extended samples were sticky upon drying and has potential to be used as adhesives.

ABSTRAK

Poliuretena serakan air telah disintesis menggunakan kaedah percampuran prepolimer serakan sonsang. Rantaian prepolimer daripada campuran isoforon diisosianat dan polipropilena glikol telah disambungkan dengan lima jenis penyambung rantaian. Dua daripadanya adalah penyambung rantaian jenis amina iaitu etilena diamina dan hidrazina manakala tiga yang lainnya adalah penyambung rantaian dari jenis diol dimana satu daripadanya berasaskan petroleum iaitu etilena glikol dan dua yang lain berasaskan sumber yang boleh diperbaharui iaitu minyak kastor dan poliol berasaskan minyak sawit. Ia sebagai langkah untuk mengurangkan tahap ketoksikan amina dengan menggantikan penyambung rantaian amina dengan diol. Selain itu, penyambung rantaian dari sumber yang boleh diperbaharui digunakan bagi mengurangkan kebergantungan terhadap sumber petroleum yang mahal dan tidak boleh diperbaharui. Analisis Spektroskopi Inframerah Transformasi Fourier menunjukkan bahawa semua sampel telah berjaya disintesis kepada poliuretena serakan air, berdasarkan penyerapan pada puncak –NH dan –karbonil uretena masing-masing di 1537-1539 cm^{-1} dan 1718-1725 cm^{-1} serta ketiadaan penyerapan gelombang NCO pada 2275 cm^{-1}. Poliuretena serakan air berasaskan minyak sawit mempunyai kelikatan yang paling tinggi iaitu 5.4 cP, bersaiz partikel 1.738 mikron tetapi mempunyai kandungan pepejal terendah iaitu sebanyak 31 wt%. Poliuretena ini juga menunjukkan kestabilan terma yang baik berbanding sampel lain. Ini dianggap berpunca daripada kandungan kumpulan hidroksil (OH) di dalam trigliserida yang berupaya untuk bertindakbalas dengan isoforon diisosianat pada suhu tinggi untuk menghasilkan poliuretena tersambung silang. Walau bagaimanapun, sampel yang disambung menggunakan penyambung rantaian berasaskan minyak sawit melekit selepas pengeringan dan mempunyai potensi untuk digunakan sebagai perekat.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CO	Castor oil
DBTDL	Dibutyl tin dilaurate
DMPA	Dimethyol propionic acid
EDA	Ethylene diamine
EG	Ethylene glycol
FTIR	Fourier transform infra red
HMDI	Hexamethylenediisocyanate
H_{12}MDI	4,4'-dicyclohexylmethane disocyanate
HYD	Hydrazine
IPDI	Isocphoronediisocyanate
MMA	Methylmetacrylate
NCO	Isocyanate group
NH	Amide group
NMP	N-methylpyrollidone
OH	Hydroxyl group
PAN	Polyacrylonitrile
PCL	polycaprolactone
PEG	Polyethylene glycol
PMMA	Polymethylmethacrylate
PPG	Polypropylene glycol
PO	Palm oil-based polyol
PU	Polyurethane
PUD	Polyurethane dispersion
TEA	Triethylamine
TGA	Thermogravimetric Analysis

CHAPTER 1

INTRODUCTION

1.1 Background

Coatings can provide materials with the desired aesthetical properties such as colour and gloss, but the vital importance is in the protection against environmental influences including moisture, radiation, biological deterioration or damage from mechanical or chemical origin. The effectiveness of protection of a material against natural deterioration depends on factors such as the quality of the coating, the substrate characteristics, the properties of the coating, and the corrosiveness of the environment (Dieterich, 1981). Most coatings such as acrylic-based, epoxy-based, polyurethane-based and alkyd-based coatings are made from petroleum-based raw materials. With the depleting resources of petroleum all around the world, scientists are forced to explore new alternatives to decrease the world's dependence on petroleum. This including Malaysian researchers have been progressively researching ways to utilise its plantations in their research as an effort to replace some petroleum-based chemicals such as polyols. Apart from castor oil and lesquerella oils which have built-in hydroxyl groups, other vegetable oils such as soy, corn, linseed and palm oils need the addition of hydroxyl at their unsaturated sites to transform them into reactive polyols (Zhang *et al.*, 2007). Many methods have been discovered to transform triglycerides of palm oil into polyols such as

glycerolysis (Tanaka *et al.*, 2008), transamidation of diethanolamine (Lee *et al.*, 2007), epoxidation (Hazimah *et al.*, 2005) and enzymatic synthesis (McNeil and Berger, 1993). These renewable polyols can be reacted with NCO group of diisocyanates to produce rigid and flexible PU foams (Guo *et al.*, 2000; Chian *et al.*, 1998), PU adhesive and coatings (Somani *et al.*, 2003; Akram *et al.*, 2008).

In coatings, PU can be found in many applications such as automotive coatings with exterior high gloss, good colour retention, good scratch and corrosion resistance (Coogan, 1997). PU coatings are also used in construction, where building floors, steel trusses and concrete supports are spray coated to make them more durable against environmental deterioration and less costly maintenance (Chattopadhyay *et al.*, 2006)

The challenge within the coating industry is to maintain or improve properties at a reasonable cost, while at the same time meeting the need for environmentally friendly coatings. Waterborne PU coating (PUD) technology is derived with this idea in mind because it exhibits low emittance of volatile organic compound (VOC) and at the same time it reduces the coating production cost by eliminating the needs to use solvents as the dispersion medium (Dieterich., 1981). The common synthesis methods to produce PUD are acetone process, prepolymer mixing technique and melt dispersion technique (Dieterich, 1981). Among these, prepolymer mixing technique is the popular choice due to little or no solvent used, imparts good quality particle dispersion and good storage stability (Weiss, 1997).

However, low molecular weight prepolymer PU particles that are dispersed in water need to be chain-extended with chain extension agents to produce higher molecular weight PU. With this technique, higher molecular weight of PU particles can be obtained without affecting bulk viscosity of the system (Oldring *et al.*, 2001). The commercial petroleum-based chain extension agents or chain extenders are ethylene diamine (EDA), hydrazine (HYD) and ethylene glycol (EG). EDA and HYD led to the formation of polyurethane-ureas, while EG resulted in the formation

of polyurethanes (Coutinho *et al.*, 2000). Thermal stability was higher when a diamine chain extender was used due to the stronger hydrogen bonding of the urea groups (Cakic *et al.*, 2009). However, diamines such as hydrazine are toxic and unstable, where a long term inhalation caused tumors (Vernot *et al.*, 1985). Their highly flammability characters have been manipulated to be used as air craft fuel and propellant by U.S Air Force (Hussain *et al.*, 2002).

1.2 Problem Statement

Strict environmental legislation on the use of solvent in coatings has driven the development of waterborne polyurethane dispersion (PUD) technology, in which harmful solvents are replaced with water as a primary dispersion medium for the polyurethane polymer. However, many PUDs still use toxic chain extenders in their synthesis. These chain extenders are usually amine based and are derived from petroleum based resources. It is well known that amines are toxic and are classified as carcinogenic and are extremely flammable. Furthermore it is derived from petroleum which is becoming an expensive and depletable commodity. This research was done as an effort to decrease the toxicity of the PUD and at the same time reducing the production cost by replacing the amine based chain extenders with vegetable oils namely castor oil and palm oil based polyol. Vegetable oils are a greener approach towards PU production since vegetable oils tends to be inexpensive, annually renewable and are available in abundance all over the world (Larock *et. al*, 2011). Castor oil is chosen due to its naturally built-in hydroxyl group in its molecular structure or in other words a naturally occurring polyol. While palm oil based polyol is chosen due to the abundance of palm trees in Malaysia. The palm oil however has to undergo chemical modification to transform it into polyol. To get more understanding on the effect of chain extenders onto PUD property, glycol-based chain extender i.e. ethylene glycol was used as comparison.

Meanwhile, to produce prepolymer, aliphatic isophorone diisocyanate (IPDI) was reacted with polypropylene glycol (PPG) in the presence of tin (II) octoate as catalyst. IPDI and PPG were chosen as basic raw materials due to their stability against oxidation and hydrolysis, respectively.

1.3 Objectives of Study

This research is designed on the following objectives:

i To synthesis waterborne polyurethane via modified prepolymer mixing method with castor oil and palm oil-based polyol as chain extenders.

ii To study the effect of different types of chain extenders on thermal stability, particle sizing, adhesion strength and hardness properties of PUD.

1.4 Scope of the Study

This research involved the preparation of PUD by utilizing castor oil and POP as chain extenders.

1. Synthesis of PUDs.
   a) Prepolymer mixing technique.
      i. IPDI, PPG, DMPA, NMP and catalyst at 80-90^{0}C in reaction vessel.
      ii. Neutralize with triethylamine (TEA) at 60^{0}C.
      iii. Calculation of NCO percentage using di-n-butyl amine back titration method.

b) Dispersion of prepolymer in deionized water.
Chain extension with CO, POP, HYD, EDA, EG.

2. Characterization and testing.
   i. Fourier transform infrared spectroscopy (FTIR).
   ii. Thermogravimetric analysis (TGA).
   iii. Viscosity measurement with a Brookfield viscometer.
   iv. Adhesion test with pencil test and hardness test.
   v. Particle size analysis.

REFERENCES

Abdul Majid, W. H., Velayutham, T. S., Ahmad, A. B., Gan, Y. K. and Gan, S. N., (2009). Synthesis and Characterization of Polyurethane Coatings Derived from

Polyols Synthesized with Glycerol, Phtalic Anhydride and Oleic Acid. *Progress In Organic Coatings.*66:367-371.

Arnoldus, R. (1990). *Surface Coating.* London: Elsevier. 179-199.

Akram, D., Ahmad, S., Sharmin, E. (2008). Synthesis, Characterization and Corrosion Protective Properties of Boron-Modified Polyurethane from Natural Polyol. *Progress in Organic Coatings.*. 63:25–32.

Cakic, S. M., Ivan R. R., Djordjevic, D. M., Stamenkovic J. V., and Stojijlkovic, D. T. (2010). Effect of the chain extender and selective catalyst on thermooxidative stability of Aqueous Polyurethane Dispersions. *Progress In Organic Coatings*. 67: 274-280.

Cakic, S. M., Stamenkovic, J. V., Djordjevic, D. M., and Ristic, I. S. (2009). Synthesis and degradation profile of cast films of PPG-DMPA-IPDI aqueous polyurethane dispersions based on selective catalysts. *Polymer Degradation and Stability*. 94, 2015-2022.

Chattopadhyay D. K., and Raju, K.V.S.N. (2006). Structural Engineering of Polyurethane Coatings for High Performance Applications. *Progress Polymer Science*.32, 352–418

Chian, K. S., and Gan, L. H. (1998) Development of Rigid Polyurethane Foam from Palm Oil, *Journal Applied Polymer Science* 68: 509-515.

Clemitson, I. (2008). *Castable Polyurethane Elastomer*. Huntersville, N.C. Taylor & Francis Group.

Coogan, R. G. (1997). Preparation and Characterization of Waterborne Polyurethane Crosslinked by Urea Bridges. *Progress in Organic Coatings*, 32: 51-63

Coutinho, F. M. B. and Delpech, M. C. (2000). *Polymer Degradation and Stability*. 70, 49-57.

Delpech, M. C., and Coutinho, F. M. B. (2000). Waterborne Anionic Polyurethane and Poly(urethane-urea): Influence of the Chain Extender on Mechanical and Adhesive Properties.

Dieterich, D. (1981). Aqueous Emulsions, Dispersions And Solutions Of Polyurethanes; Synthesis And Properties. *Progress in Organic Coating.* 9: 281 – 340

Dong, H. J., Eun, Y. K., Young, S. K., and Byung, K. K. (2010). High Solid and High Performance UV Cured Waterborne Polyurethanes. *Colloids and Surfaces A: Physicochem. Eng. Aspects*. 370: 58-63.

Fernanda, O. V. D. C., Diogo, H. R. M., Vinicus, B. V. and Forte, M. M. C. (2004). Study of Castor Oil Polyurethane-Polymethylmethacrylate Semi Interpenetrating Polymer Network (SIPN) Reaction Parameters Using a 2^3 Factorial Experimental Design. *Material Research*. Vol 7: 4: 539-543.

Forrest, M. J. (1999). Chemical Characterisation of Polyurethane. United Kingdom. iSmithers Rapra Publishing.

Guo, A., Javni, I., and Zoran, P. (2000). Rigid Polyurethane Foams Based on Soybean Oil. *Journal of Applied Polymer Science*. 77: 467-473

Harjunalanen, T. and Lahtinen, M. (2003). *European Polymer Journal.* 39: 817-824.

Harrington, R., and Hock, K. (1998). *Flexible Polyurethane Foams*, 2nd ed. Midland, MI: Dow Chemical Company.

Hazimah, A. H., Hoong, S. S., Mohd Norhisham S., Tuan Noor Maznee, T. I., Ooi T. L., Salmiah A., Friebel S., Philipp C. and Hora G. (2005). Palm-Based Polyol for Adhesives. *MPOB Information Series*. Issn 1511-7871.

Hoong S. S., Hazimah A. H., Mohd Norhisham S., Tuan Noor Maznee T. I., Ooi T. L., Salmiah A., Friebel S., Philipp C. and Hora G. (2007). Palm-Based Polyol for Coatings. *MPOB Information Series. Issn* 1511-7871.

Hoong S. S., Hazimah A. H., Mohd Norhisham S., Tuan Noor Maznee T. I., Salmiah A., Nurul Ain H., Kosheela Devi P (2008). Preparation of Low Viscosity and Light Coloured Fatty Acid Based Polyol. *Journal of Palm Oil Research*. 44-52.

Hussain, S. M., and Frazier, J. M. (2002). Cellular Toxicity of Hydrazine in Primary Rat Hepatocytes. *Toxicological Sciences*, (2002), 69, 2, 424-432.

Jaudouin, O., Robin, J. J., Lopez-Cuesta, J. M., Perrin, D., and Imbert, C. (2012). Ionomer-Based Polyurethanes: A Comparative Study of Properties and Applications. *Polymer International*. 61: 495-510.

Jhon, Y. K, Cheong, I. W. and Kim J. H. (2001). Chain Extension Study of Aqueous Polyurethane Dispersion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 179: 71-78

Kim, B. K., Kim, T. K., and Jeong, H. M. (1994). Aqueous Dispersion of Polyurethane Anionomers from H_{12}MDI/IPDI, PCL, BD, and DMPA. *Journal of Applied Polymer Science.* 53: 371–8.

Kim, B. K., Yang, J. S., Yoo, S. M., and Lee, J. S. (2003). Waterborne polyurethanes containing ionic groups in soft segment. *Colloid Polymer Science*. 281: 461-468.

Kloss, J., Munaro, M., DeSouza, G. B., Gulmine, J. V, Wang, S. H., Zawadki, S. and Akcelrud, L. (2002). Poly(ester urethane)s with polycaprolactone soft segments: A morphological study. *Journal of Polymer Science: Part A: Polymer Chemistry*, 2002, 40, 4117 – 4130.

Kundu, P. P., and Sharma, V. (2008). Condensation Polymers from Natural Oils. *Progress in Polymer Science*. 33: 1199–1215

Kurt, C. F. Jr. (1962). Chemistry and Technology of Polyurethane, *High Polymers, Technology*. Interscience Publishers, New York, Vol. XVI, Part II.

Larock, R. C., Pfister, D. P., and Ying Xia. (2011). Recent Advances in Vegetable Oil-Based Polyurethanes. *Chem SusChem*. 4: 703-717

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 Material Science*. 84:1161-116.

Lee, H. T., and Wang, C. C. (2005). Synthesis and Properties of Aqueous Polyurethane/polytert-butylacrylate Hybrid Dispersions. *Journal of Polymer Research*. 12: 271-277

Li, H. B., Yun, J. L. and Shu, F. Z. (2006). Synthesis and Properties of Waterborne Polyrurethane Dispersions with Ions in the Soft Segments. *Journal of Polymer Research*. 13: 507-514.

Majid, R.A., Hourston D. J., and Satguru, S. (2011), Nanostructured urethane-acrylic hybrid dispersion: polymer synthesis and technology. Book (ISBN-10: 3846594989) Lambert Academic Publishing, GmbH & Co. KG, Saarbrücken, Germany

Mallu, P., Siddaramaiah and Somashekar (2000). Synthesis and Characterization of Castor Oil Based Polyurethane-Polyacrylonitrile Interpenetrating Polymer Networks. *Bulletin of Material Science.* Vol 23: 5: 413-418

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 Biotechnolology*. 7:75–87.

Oldring, P. K. T., and Tuck, N. (2001). *Resins for Surface Coatings*, 2nd ed, vol. 3. London: John Wiley and Sons / SITA Technology.

Pannone, M. C., and Macosko, C. W. (1987). Kinetics of Isocyanate Amine Reactions. *Journal of Applied Polymer Science*. 34: 2409-2432.

Patel, A., Patel, C., Patel, M. G., Patel, M., and Dighe A. (2009). Fatty Acid Modified Polyurethane Dispersion for Surface Coatings: Effect of Fatty Acid Content and Ionic Content. *Progress in Organic Coatings.* 2355

Rahman, M. M., Han, D. K. and Won, K. L. (2009). Properties of Crosslinked Waterborne Polyurethane Adhesive with Modified Melamine: Effect of Curing Time, Temperature and HMMM Content. *Fibers and Polymers*. 10: 6-13.

Saunders, J. H. (1959). The Reactions of Isocyanates and Isocyanates Derivatives at Elevated Temperatures. *Rubber Chemistry and Technology*. 32: 337-345.

Sardon H., Irusta L., Fernandez-Berridi, M. J., Luna, J., Lansalot, M. and Bourgeat-Lami E. (2011). Waterborne Polyurethane DispersionObtained by the Acetone Process: A Study of Colloidal Features. *Journal of Applied Polymer Science*. 120: 2054-2062

Sebenik, U. and Krajnc M. (2004). Seeded semibatch emulsion copolymerization of methyl methacrylate-polyurethane. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2004, 233, 51-62.

Segura, D. M., McCourt N. A., Phelps, R., and Segura, A. (2005). Chemistry of Polyurethane Adhesives and Sealants. *Handbook of Adhesives and Sealants*. Elsevier Ltd.

Somani K. P., Kansara, S. S., Patel N. K., and Rakshit, A. K. (2003) Castor Oil Based Polyurethane Adhesives for Wood-to-Wood Bonding. *International Journal of Adhesion and Adhesives*. 23:269–75.

Tanaka, R., Shigeo, H., and Hyoe, H. ((2008). Preparation and characterization of polyurethane foams using a palm oil-based polyol. *Bioresource technology*. 99: 3810-3816

Tuan Noor Maznee. T I; Hazimah, A H; Ooi, T L And Salmiah, A (2007). Polyol from Used Frying Oil (P-Ufo*). MPOB Information Series*. Issn 1511-7871.

Uldis S., Sevastyanova I., Misane M., Cabulis, U., and Beverte, I. (2006). Structure and Properties of Polyurethane Foams Obtained from Rapeseed Oil Polyol. *Proceedings of Estonian Academy of Sciences Chemistry*. 55: 101-110

Velankar, S. and Cooper, S. L. (2000). Microphase separation and rheological properties of polyurethane melts. Part 2: Effect of block incompatibility on the microstructure *Macromolecules*. 33: 395-403.

Vernot, E. H., MacEwen, J. D., Bruner, R. H., Haun, C. C., Kinkead, E. R., Prentice, D. E., Hall, A., Schmidt, R. E., Eason, R. L., Hubbard, G. B. and Young, J. T. (1985). Long-term inhalation toxicity of hydrazine. *Fundamental and Applied Toxicology*. 5, (6):1050–1064.

Wen, T.C., Wang, Y. J., Cheng, T. T., and Yang C.H. (1999). Waterborne Polyurethane Single-ion Electrolyte from Aliphatic Diisocyanate and Various Molecular Length of Polyethylene glycol. *Polymer*. 40: 3979-3988

Weiss, K. D. (1997). Paints and Coating: A mature Industry in Transition. *Progress in Polymer Science.* 22: 203-245.

Wicks, D. A., and Ajaya K. N. (2006). The Influence of the Ionic Concentration of the Polymer Degree of Neutralization and Chain Extension on Aqueous Polyurehane Dispersions Prepared by the Acetone Process. *Polymer*. 47: 1805-1811.

Zhang, L., Hyun, K. J., Malsam, J., Herrington, R., and Macosko, C. W. (2007). Substituting Soybean Oil-Based Polyol into Polyurethane Flexible Foams, *Polymer* . 48: 6656-6667.