UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERISATION OF JATROPHA OIL-BASED WATERBORNE POLYURETHANE DISPERSIONS

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By

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

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March 2016

Chairman : Professor Luqman Chuah Abdullah, PhD
Faculty : Engineering

The transition from solvent-borne to waterborne polyurethane (PU) coatings is driven by the stringent regulations to reduce emissions of volatile organic compounds (VOCs) from the products, enhanced by the increasing awareness of the consumers of safety and health issues. On the other hand, a low cost, abundant, and renewable vegetable oil source is now receiving increasing attention for polyurethane production. Previous studies reported the possibility of the production of PU coatings, adhesives and elastomers from non-edible jatropha oil. However, as far as is known, no study has reported on waterborne PU synthesis from jatropha oil. In this research, jatropha oil is modified to polyol to be used as a starting material for the production of a waterborne PU dispersion. A series of jatropha oil-based polyols (JOLs) were synthesised from jatropha oil by a two-step process, namely epoxidation and oxirane ring opening. The effect of epoxidation conditions on the properties of the JOLs was investigated. The JOLs are liquid under room conditions with a hydroxyl number in a range of 138 to 217 mg KOH/g.

The jatropha oil-based waterborne polyurethane (JPU) dispersions were produced by polymerising the JOLs with isophrene diisocyanate (IPDI) and dimethylol propionic acid (DMPA). The colloidal stability of the resulting JPU dispersions were studied by particle size analysis and rheology measurements. Inclusion of up to 5.4 wt.% of DMPA as an internal emulsifier produced a wide range of particle sizes from 84 nm to 825 nm. However, further increasing the DMPA content up to 6.8 wt.% resulted in smaller particles but a multimodal particle size distribution was obtained for the dispersion synthesised from low OH number polyol. The dispersions have a solid content of 22.9 to 26.9 wt.% with a relatively low viscosity in the range 5.6-53.1 mPa.s. The JPU dispersions exhibited the typical flow behaviour of the commercial polyurethane dispersions, ranging from almost Newtonian to a shear thinning fluid, and the experimental data correlated well with the Cross model. The samples were stable after 18 months of storage under room conditions.

A films with up to 62 wt.% bio-based content were successfully produced after evaporation of water from the JPU dispersion. The chemical, physical, mechanical and thermal properties of the films were characterised. The experimental data revealed that the OH number of the JOLs, DMPA content and the hard segments were the key parameters which control the structure and the properties of the JPU films. The JPU film derived high OH number polyol and high hard segment content exhibited the highest crosslinking density. This contributed to higher hardness, better mechanical properties, and hydrophobic surface character. The films show an elastomeric polymer behaviour and good thermal stability.

The JPU dispersions were applied on a wood surface and the performance of the coatings were evaluated. The JPU films have excellent adhesion to the substrate, excellent optical properties as well as chemical and abrasion resistance. The PU dispersions synthesised in this work possess good properties with a promising application as a standalone coating or binder for wood and decorative coatings.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS DAN PENCIRIAN DISPERSI POLIURETANA BERBASIS AIR YANG BERASASKAN MINYAK JATROPHA

Oleh

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Peralihan daripada poliuretana (PU) berbasis pelarut kepada dispersi PU berbasis air adalah didorong oleh peraturan ketat untuk mengurangkan pembebasan sebatian organik meruap (VOC) daripada produk, ditambah pula dengan peningkatan kesedaran pengguna mengenai isu-isu keselamatan dan kesihatan. Minyak sayuran yang merupakan sumber boleh diperbaharui dan boleh diperolehi dengan harga yang murah kini mendapat perhatian utama dalam penghasilan PU. Kajian lepas mendapati minyak jatropha boleh digunakan untuk membuat bahan penyalut, perekat dan elastomer. Walaubagaimanapun, tiada kajian dilaporkan mengenai pembuatan dispersi PU berbasis air daripada minyak jatropha. Dalam kajian ini, minyak jatropha diubah suai kepada poliol untuk digunakan sebagai bahan untuk pembuatan PU berbasis air. Satu siri poliol telah dihasilkan melalui dua langkah, iaitu pengepoksidaan dan pembukaan cincin oksiran. Kajian dilakukan untuk mengenalpasti kesan kondisi epoksidasi terhadap sifat poliol yang dihasilkan. Hasil ujikaji mendapati semua JOL bersifat cecair pada keadaan bilik dengan nilai nombor hidroksil antara 138 hingga 217 mg KOH/g.

Dispersi PU berbasis air yang berasaskan minyak jatropha (JPU) telah berjaya dihasilkan melalui tindak balas pempolimeran antara JOL dengan isoprena diisosianat (IPDI), dan dimetilol asid propionik (DMPA). Kestabilan koloid JPU dalam air dikaji melalui analisis saiz partikel dan juga reologi. Penambahan sehingga 5.4% DMPA sebagai pengemulsi dalaman menghasilkan pelbagai saiz partikel daripada 84 nm hingga 825 nm. Apabila kandungan DMPA ditingkatkan sehingga 6.8 %, partikel yang lebih kecil terhasil tetapi beberapa mod taburan saiz partikel telah diperolehi bagi JPU yang disintesis daripada poliol dengan nombor OH yang rendah. Semua JPU ini disediakan dengan kandungan berat pepejal 22.9-26.9 %, dan kelikatan yang rendah dalam julat 5.6-53.1 mPa.s. JPU ini mempamerkan kelakuan dispersi poliuretana komersial, iaitu sama ada hampir Newtonian atau *shear-thinning*, dan data eksperimen ini boleh diwakili oleh model Cross. Sampel JPU didapati stabil di bawah 18 bulan penyimpanan pada keadaan bilik.

Filem yang mengandungi sehingga 62% berat kandungan berasaskan bio telah berjaya dihasilkan selepas air disejatkan dari dispersi JPU. Ini menunjukkan kebolehan pembentukan filem yang baik. Sifat-sifat kimia, fizikal, mekanikal dan haba filem yang terhasil telah ditentukan. Data eksperimen menunjukkan bahawa kandungan kumpulan berfungsi OH pada JOL, DMPA dan segmen keras adalah parameter utama yang mengawal struktur dan sifat-sifat filem JPU. Filem yang disintesis daripada poliol yang memiliki nombor OH tertinggi dan juga tinggi kandungan segmen kerasnya mempamerkan ketumpatan silang yang paling tinggi, seterusnya menyumbang kepada kekerasan yang lebih tinggi, sifat mekanikal yang lebih baik, dan mempamerkan permukaan hidrofobik. Semua filem JPU mempamerkan kelakuan polimer lentur mempunyai kestabilan terma yang tinggi.

Dispersi JPU berbasis air telah digunakan sebagai bahan pelapis untuk kayu dan prestasi lapisan tersebut dinilai. JPU juga merekat sempurna terhadap substrat kayu JPU juga merekat sempurna terhadap substrat kayu. Selain itu, lapisan tersebut mempamerkan ciri-ciri optik yang sangat baik, begitu juga dengan rintangan kimia dan rintangan lelasannya. Keseluruhannya, dispersi JPU berbasis air yang telah disintesis dalam kajian ini mempunyai ciri-ciri yang baik dan berpotensi digunakan sebagai bahan pelapis atau pengikat untuk formulasi bahan pelapis kayu dan hiasan.

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I certify that a Thesis Examination Committee has met on 31 March 2016 to conduct the final examination of Sariah binti Saalah on her thesis entitled "Synthesis and Characterisation of Jatropha Oil-Based Waterborne Polyurethane Dispersions" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Standard for Testing Material
ATR	Attenuated total reflectance
CAGR	Compound annual growth rate
DMA	Dynamic Mechanical Analysis
DMPA	Dimethylol propionic acid
DSC	Differential Scanning Calorimeter
DTG	Derivative of thermogravimetric (TG) curve
E	Young's modulus
E'	Storage modulus (tension mode)
E"	Loss modulus (tension mode)
E_a	Activation energy
EDA	Ethylene diamine
EJO	Epoxidised jatropha oil
EW	Equivalent weight
FTIR	Fourier Transform Infrared
G'	Storage modulus (shear mode)
G"	Loss modulus (shear mode)
GPC	Gel permeation chromatography
HDA	1-6 Hexanediamine
HEMA	2-Hydroxyethyl methacrylate
H_{12}MDI	4-4 dicyclohexylmethane diisocyanate
IPDI	Isophrene (or isophorone) diisocyanate
IV	Iodine value
JO	Jatropha oil
JOL	Jatropha oil-based polyol
JPU	Jatropha oil-based waterborne polyurethane
MDI	Diphenylmethane diisocyanate
MFFT	Minimum film forming temperature
OOC	Oxirane oxygen content (%)
OOC_{th}	Theoretical oxirane oxygen content (%)
PU	Polyurethane

SEM	Scanning Electron Microscope
TEA	Triethylamine
TDI	Toluene diisocyanate
TGA	Thermogravimetric Analysis
ZP	Zeta potential (mV)
d_{50}	Average particle size (nm)
gram/eq	Gram per equivalent
M_c	Molecular weight between crosslink
M_n	Number average molecular weight (Dalton)
M_w	Weight average molecular weight (Dalton)
^{n}	Flow index behavior
OH	Hydroxyl
R	Universal gas constant
Tan δ	Damping, ratio of E"/E'
T_g	Glass transition temperature (°C)
σ	Tensile strength (MPa)
B	Titration of blank (mL)
ε	Elongation at break (5)
η	Viscosity (mPas)
η*	Complex viscosity (mPas)
N	Normality
W	Weight (g)
S	Titration of the sample (mL)
f	Functionality
ω	Angular frequency (s^{-1})
ρ_2	Density of dry polymer
γ	Shear rate (s^{-1})
δ	Solubility parameter
v_1	Molar volume of solvent
υ_e	Crosslinking density
$\emptyset_2$	Volume fraction of polymer in the swollen network
χ_{12}	Polymer–solvent interaction parameter

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Polyurethane (PU) is a versatile polymer which has been employed in a wide range of applications, such as coatings, adhesives, sealants, foams, elastomers, and others. With a proper selection of reactant, PU ranges from high performance elastomers to tough and rigid plastics can be easily fabricated (Lu & Larock, 2008). PU based coatings have an established place in the coatings industry due to the high level of quality such as outstanding chemical and corrosion resistance, excellent abrasion resistance, low temperature flexibility, high toughness, and a wide range of mechanical strength (Kong, et al., 2013; Melchiors et al., 2000). Basically, polyurethane backbone structures consist of a soft segment from polyol, and a hard segment from isocyanate. The hard segments govern the hardness, strength and toughness of the PU films, while the soft segments determine the flexibility and glass transition temperature. The versatile mechanical properties of PU arise from phase separation of the thermodynamically incompatible hard and soft segments, which arrange themselves in microdomains as a result of a hydrogen bonding bridge between the urethane groups (Kanda et al., 2008). The hydrogen bridge bond forms a stable physical network, ensuring the outstanding mechanical properties of the PU film, while the urethane groups helps to protect the polymer chain against solvents, acids, bases and other chemicals (Melchiors et al., 2000).

Traditional PU coatings have been diluted with an organic solvent that helps to carry the coatings from the applicator to the substrate. Organic solvents often contain volatile organic compounds (VOCs). The emission of VOCs during the formulation of coatings, inks, and paints has caused a wide variety of air quality problems (Nanda & Wicks, 2006). With enforcement of stringent regulations aimed at preventing pollution, such as the Clean Air Act, the application of solvent-borne coatings has been phased out and replaced with coatings free of VOCs such as waterborne coatings and ultraviolet (UV) curable coatings (100 % solid) (Athawale & Kulkarni, 2010; DeVito, 1999; Ristić et al., 2012). In Europe, waterborne technology has been accepted as it has become the largest volume of coatings particularly in terms of decorative coatings (Scrinzi et al., 2011). These products fulfil many of the requirements related to conventional solvent-borne coatings, e.g., low viscosity at a high molecular weight and good applicability (Cakić et al., 2013). The transition from solvent-borne to waterborne PU may lower the manufacturing costs associated with solvent cost, and reduce the health and fire risks (Garrison et al., 2014). It has been forecast that the global PU dispersion market will grow at a CAGR of 7.5 % in the years 2012 to 2018, with the market value estimated to be worth US $ 1.18 billion by 2018 (Transparency Market Research, 2015b).

Waterborne polyurethane (PU) dispersion is a typical colloid system consisting of PU particles stabilised in a continuous water phase. In preparing a waterborne PU dispersion, ionomers which contain hydrophilic groups are incorporated into the side chain or the backbone of the polymer to enable dispersibility of the water-insoluble polyurethane. Anionic ionomers such as dimethylol propionic acid (DMPA) act as an emulsifier to provide dispersion stability for longer storage of the waterborne PU dispersion. Currently, most waterborne PU dispersions are derived from a petroleum based polyol which is non-renewable. As fossil resources become depleted, coupled with awareness of environmental issues related to non-biodegradable products, utilisation of more sustainable and environmentally friendly raw materials for fabrication of bio-based polymers is gaining increasing attention. Recently, the successful synthesis of waterborne PU dispersions from vegetable oil based polyol derived from soybean oil, castor oil, rapeseed oil and linseed oil has been reported (Chang & Lu, 2013; Lu & Larock, 2008; Ni et al., 2010). However, to the best of the knowledge of the authors, no research has been reported on the production of waterborne PU dispersions from non-edible jatropha oil. In Malaysia, jatropha has become one of the most important crops after palm oil and rubber, mainly planted for biodiesel production. BATC Development Berhad has been actively engaged in jatropha plantation and the bio-fuel industry since 2007. Up to 2011, about 600,000 acres of planted area, 3.3 million acres in landbanks and more than 300 nurseries and collection centres were reported in Malaysia (Bionas, 2011).

Jatropha oil (JO) which is extracted from the seeds of the jatropha fruit is a promising candidate for chemical purposes as it contains 78.9 % unsaturated fatty acids, mainly of oleic acid (43.1 %) and linoleic acid (34.4 %) (Sarin et al., 2007). This high degree of unsaturation provides a broad alternative for chemical modification to produce polymers with the desired properties. Furthermore, the utilisation of a non-edible jatropha oil will reduce the dependency on edible oils for chemical purposes (Rios et al., 2011). Previous research has revealed the potential usage of jatropha oil for production of various polymers with promising properties such as alkyd resin, PU coatings, PU adhesive and PU elastomer (Aung et al., 2014; Boruah et al., 2012; Harjono et al., 2012; Hazmi et al., 2013). In this research, an attempt is made to extend the potential of jatropha oil as a starting material for the production of a waterborne PU dispersion.

1.2 Problem statement

Malaysia is among the largest of the world's producers of palm oil. In the coating industry, successful utilisation of such oil has been reported to produce alkyd resin, epoxy palm oil, oleic acid acrylate resin and PU acrylate for wood coatings and overprint varnish applications (Rozman et al., 2013). Due to the low unsaturation in palm oil composition, production of a coating polymer from palm oil is more towards ultra-violet (UV) curable acrylate resin from palm oil derivatives such as oleic acid and palm oil monoglyceride (Rozman et al., 2013; Salleh et al., 2010; Wan Rosli et al., 2003). Realising the importance of reducing the dependency on edible oil for polymer fabrication, the non-edible jatropha oil is a new alternative. With almost 80 % unsaturated fatty acids, the double bond in the oil triglyceride structure could be directly functionalised to hydroxyl in polyol preparation.

Generally, vegetable oil with a high degree of C=C unsaturation will result in a high OH number polyol for crosslinking with isocyanate to produce polyurethane with good mechanical properties (Meier et al., 2007). The fatty acid composition of the starting vegetable oil and the polyol production method determine the properties of the final polyol such as OH number, molecular weight and rheology. As the polyol and isocyanate are the main ingredients in PU, the higher amount of polyol loading will increase the bio-based content. Typically, up to 60 wt.% bio-based content has been reported (Lu & Larock, 2008). Therefore, depending on the specific application, the properties of the PU could be tailored by varying the OH number of the polyol. The OH numbers will determine the appropriate amount of hard segment required for polymerisation. If a high bio-based PU is targeted, a low OH functionality polyol is selected, but the final film properties should be considered. The non-functional groups in the polyol may result in a tacky product which is undesirable for coating applications, but may be a characteristic of a pressure sensitive adhesive (Wool, 2005). On the other hand, the high functionality of some vegetable oil polyols may gel during polymerisation due to the higher crosslinking and therefore present potential difficulties in dispersing the PU prepolymers into water (Lu & Larock, 2008).

It is worth mentioning that the properties of the polyol also depend on the production method. As far as an industrially important two-step method, i.e. epoxidation followed by oxirane ring opening route, is concerned, various parameters should be controlled at each consecutive stage (Goud et al,, 2010; Saurabh et al., 2011). Therefore, it is very important to conduct a systematic study of the effect of epoxidation parameters on the properties of jatropha oil-based polyol especially the OH numbers, as these will affect the properties of the waterborne polyurethane dispersions in the wet colloidal state as well as in the dry film state.

In general, the characteristics of the colloidal dispersions do not directly affect the mechanical properties of the resulting dry films. However, information on the colloidal stability and rheology of the dispersion is important with respect to storage and application. For example a low viscosity and molecular weight independent of the dispersed polymer is necessary for spray applications, but low zero shear rate viscosity is subject to sedimentation of the PU particles upon storage (Duffy, 2015; Kastner, 2001). A few factors have been reported to affect the stability of colloidal PU dispersions such as the degree of neutralisation and the stirring procedure. However, these are less important when compared to the ionic emulsifier content (Philipp & Eschig, 2012). The

ionic groups in the DMPA are reported to improve the mechanical properties, but tend to make the dispersion film more sensitive to water and chemicals (Bullermann et al., 2013). Therefore, the amount of DMPA should be controlled to be as low as possible yet sufficient to stabilise the PU particles upon storage. In addition, a balanced composition between soft segment (polyol) and the hard segment in the PU formulation is an important criterion to determine the mechanical properties of the polymers (Ni et al., 2010).

In this study, jatropha oil based waterborne PU dispersions will be prepared and characterised. The effect of polyol OH number, DMPA content and hard segment content with the stability of the wet jatropha oil-based polyurethane (JPU) dispersion and the physical, mechanical and thermal properties of the dry JPU films will be studied. On the other hand, the performance of the JPU dispersion as wood coatings will be evaluated. These properties will have an influence on the practical design of products as the PU dispersion can be used as a standalone coating or as a binder in wood and decorative coatings.

1.3 Objectives of the study

The main objective of this study is to investigate feasibility of producing jatropha oil-based waterborne polyurethane dispersions for coating applications. To achieve this objective, specific objectives have been identified:

a. To investigate the effect of epoxidation conditions (molar ratio, time, temperature) on the properties of jatropha oil-based polyol.
b. To investigate the effect of hard segment, hydroxyl number, and ionic emulsifier content on the colloidal stability and rheological properties of jatropha oil-based waterborne polyurethane dispersions.
c. To relate the effect of hard segment, hydroxyl number and ionic emulsifier content on the physical, mechanical and thermal properties of jatropha oil-based waterborne polyurethane films.
d. To evaluate the coating performance of jatropha oil-based waterborne polyurethane.

1.4 Scope of the study

The scope of the study can be expressed as follows.

a. Preparation of jatropha oil based polyol by epoxidation and oxirane ring opening. Two series of epoxidised jatropha oil (EJO) to be obtained by varying the molar ratio formic acid to oil double bond from 0.4 to 1.0, at different temperatures, 50 °C and 60 °C. The third series to be produced at a fixed molar ratio of 0.6, temperature of 60 °C but with different reaction times. Only the third series will be selected for the oxirane ring opening step to produce jatropha oil-based polyols (JOL). The chemical and rheological properties of the EJO and JOL are to be investigated.
b. Preparation of a jatropha oil based waterborne polyurethane (JPU) dispersion by the acetone method. Two group samples will be prepared: 1) a fixed molar

ratio with varied hard segment (34-45 wt.%), and 2) a fixed hard segment at 45 wt.%.

c. The colloidal stability of the JPU dispersion is to be evaluated by particle size analysis as well as rheological analysis.
d. The chemical, physical, mechanical and thermal properties of the JPU films are to be investigated and correlated with the composition of the JPU. Four samples will be selected for a coating application on wood substrate, and the performance of the coatings evaluated.

In this study, a waterborne JPU dispersion with properties that are comparable to a commercial PU dispersion is targeted. The specification of the commercial waterborne petro-based PU dispersion is provided in Table 1.1.

Table 1.1. Specification of commercial PU dispersion (Adapted from Kamsons Chemicals Pvt. Ltd. (n.d.))

Product name: Kamthane K-1432	
Type	Anionic, aliphatic
Appearance	Milky white
Total solids (% w/w)	38
pH	7.0-8.5
Viscosity (mPa.s)	30-90 (at 30 °C)
Elongation at break (%)	550
Konig hardness (s)	40

1.5 General overview of the thesis

The thesis is organised in five chapters. The first chapter provides the background of the research with an introduction to the waterborne polyurethane, followed by the problem statement, as well as the objectives and the scope of the present research.

In the second chapter, literature related to the modification of vegetable oil to polyol as well as the previous study on waterborne polyurethane is reviewed.

The third chapter focuses on the materials and methodology involved in the multistage preparation and characterisation of waterborne polyurethane from jatropha oil.

Chapter four covers the results and discussion of all experimental works. To facilitate the reading, the chapter is divided into four parts; 1) Production of jatropha oil-based polyol by epoxidation and oxirane ring opening, 2) Synthesis, stability and rheology of jatropha oil-based waterborne polyurethane dispersion, 3) Properties of jatropha oil-based waterborne polyurethane films, and 4) Performance of the waterborne polyurethane as wood coating.

Finally, the conclusions and recommendations are summarised in Chapter five.

REFERENCES

Ahmad, S. (2002). Palm-based Polyols and Polyurethanes. *MPOB Technology*, *24*, 1–29.

Akbar, E., Yaakob, Z., Kamarudin, S. K., Ismail, M., & Salimon, J. (2009). *Characteristic and Composition of Jatropha Curcas Oil Seed from Malaysia and its Potential as Biodiesel Feedstock Feedstock* (Vol. 29).

Alam, M., Akram, D., Sharmin, E., Zafar, F., & Ahmad, S. (2014). Vegetable oil based eco-friendly coating materials: A review article. *Arabian Journal of Chemistry*, *7*(4), 469–479.

Argyropoulos, J., Popa, P., Spilman, G., Bhattacharjee, D., & Koonce, W. (2009). Seed oil based polyester polyols for coatings. *Journal of Coatings Technology and Research*, *6*(4), 501–508.

Asif, A., & Shi, W. (2004). UV curable waterborne polyurethane acrylate dispersions based on hyperbranched aliphatic polyester: effect of molecular structure on physical and thermal properties. *Polymers for Advanced Technologies*, *15*(11), 669–675.

Asif, A., Shi, W., Shen, X., & Nie, K. (2005). Physical and thermal properties of UV curable waterborne polyurethane dispersions incorporating hyperbranched aliphatic polyester of varying generation number. *Polymer*, *46*(24), 11066–11078.

Athawale, V. D., & Kulkarni, M. a. (2010). Polyester polyols for waterborne polyurethanes and hybrid dispersions. *Progress in Organic Coatings*, *67*(1), 44–54.

Aung, M. M., Yaakob, Z., Kamarudin, S., & Abdullah, L. C. (2014). Synthesis and characterization of Jatropha (Jatropha curcas L.) oil-based polyurethane wood adhesive. *Industrial Crops and Products*, *60*, 177–185.

Ayres, E., Oréfice, R. L., & Yoshida, M. I. (2007). Phase morphology of hydrolysable polyurethanes derived from aqueous dispersions. *European Polymer Journal*, *43*(8), 3510–3521.

Bionas. (2011). BATC Development Company Profile., pp. 1–26, Retrieved from http://bionas-usa.com/file/BATC%20%20Company%20Profile.pdf

Blayo, A., Gandini, A., & Le Nest, J.-F. (2001). Chemical and rheological characterizations of some vegetable oils derivatives commonly used in printing inks. *Industrial Crops and Products*, *14*(2), 155–167.

Boruah, M., Gogoi, P., Adhikari, B., & Dolui, S. K. (2012). Preparation and characterization of Jatropha Curcas oil based alkyd resin suitable for surface coating. *Progress in Organic Coatings*, *74*(3), 596–602.

Bulian, F., & Tiberio, M. (2009). Market Needs and End Uses (2) – Industrial Wood Coatings. In *Wood Coatings: Theory and Practice* (pp. 233–258).

Bullermann, J., Friebel, S., Salthammer, T., & Spohnholz, R. (2013). Novel polyurethane dispersions based on renewable raw materials—Stability studies by variations of DMPA content and degree of neutralisation. *Progress in Organic Coatings*, *76*(4), 609–615.

Caillol, S., Desroches, M., Boutevin, G., Loubat, C., Auvergne, R., & Boutevin, B. (2012). Synthesis of new polyester polyols from epoxidized vegetable oils and biobased acids. *European Journal of Lipid Science and Technology*, *114*(12), 1447–1459.

Cakić, S. M., Ristić, I. S., & Ristić, O. Z. (2012). Thermal Analysis of Polyurethane Dispersions Based on Different Polyols. In F. Zafar & E. Sharmin (Eds.), *Polyurethane* (pp. 79–100). InTech.

Cakić, S. M., Špírková, M., Ristić, I. S., B-Simendić, J. K., M-Cincović, M., & Poręba, R. (2013). The waterborne polyurethane dispersions based on polycarbonate diol: Effect of ionic content. *Materials Chemistry and Physics*, *138*(1), 277–285.

Cakic, S. M., Stamenkovic, J. V., Djordjevic, D. M., & 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*(11), 2015–2022.

Chang, C., & Lu, K. (2012). Natural castor oil based 2-package waterborne polyurethane wood coatings. *Progress in Organic Coatings*, *75*, 435–443.

Chang, C.-W., & Lu, K.-T. (2013). Linseed-oil-based waterborne UV/air dual-cured wood coatings. *Progress in Organic Coatings*, *76*(7-8), 1024–1031.

Chattopadhyay, D. K., & Raju, K. V. S. N. (2007). Structural engineering of polyurethane coatings for high performance applications. *Progress in Polymer Science*, *32*(3), 352–418. doi:10.1016/j.progpolymsci.2006.05.003

Chen, R. (2014). *Bio-based materials from vegetable oils*. (Doctoral dissertation). Iowa State University, Ames, Iowa). Paper 13709

Chen, R., Zhang, C., & Kessler, M. R. (2014a). Anionic waterborne polyurethane dispersion from a bio-based ionic segment. *RSC Advances*, *4*(67), 35476.

Chen, R., Zhang, C., & Kessler, M. R. (2014b). Anionic Waterborne Polyurethane Dispersion from Bio-based Ionic Segment. *RSC Advances*, *4*, 35476–35483.

Coogan, R. G. (2000). Post-crosslinking of water-borne urethanes, *32*(December 1996), 51–63.

Dai, H., Yang, L., Lin, B., Wang, C., & Shi, G. (2009). Synthesis and Characterization of the Different Soy-Based Polyols by Ring Opening of Epoxidized Soybean Oil with Methanol, 1,2-Ethanediol and 1,2-Propanediol. *Journal of the American Oil Chemists' Society*, *86*(3), 261–267.

Dave, V. J., & Patel, H. S. (2013). Synthesis and characterization of interpenetrating polymer networks from transesterified castor oil based polyurethane and polystyrene. *Journal of Saudi Chemical Society*, 1–7.

Davies, W. (1990). Some property aspects of aqueous polyurethane ionomer dispersions. In D. R. Kansa (Ed.), *Additives for water-based coatings* (pp. 181–209). The Royal Society of Chemistry.

Deka, H., & Karak, N. (2009). Bio-based hyperbranched polyurethanes for surface coating applications. *Progress in Organic Coatings*, *66*(3), 192–198.

Delpech, M. C., & Coutinho, F. M. . (2000). Waterborne anionic polyurethanes and poly(urethane-urea)s: influence of the chain extender on mechanical and adhesive properties. *Polymer Testing*, *19*(8), 939–952.

Denny, J. (2014). Shifting production in CASE market highlighted at conference. *Utech-polyurethane.com*. Retrieved May 9, 2016, from http://utech-polyurethane.com/information/shifting-production-in-case-market-highlighted-at-conferencecase/

Desroches, M., Escouvois, M., Auvergne, R., Caillol, S., & Boutevin, B. (2012). From Vegetable Oils to Polyurethanes: Synthetic Routes to Polyols and Main Industrial Products. *Polymer Reviews*, *52*, 38–79.

DeVito, S. C. (1999). Present and future regulatory trends of the United States environmental protection agency. *Progress in Organic Coatings*, *35*(1-4), 55–61.

Duffy, J. (2015, January). Controlling Suspension Rheology. *Chemical Engineering*, 34–39.

Fang, C., Zhou, X., Yu, Q., Liu, S., & Guo, D. (2014). Synthesis and characterization of low crystalline waterborne polyurethane for potential application in water-based ink binder. *Progress in Organic Coatings*, *77*, 61–71.

Flickinger, G. L., Dairanieh, I. S., & Zukoski, C. F. (1999). The rheology of aqueous polyurethane dispersions. *Journal of Non-Newtonian Fluid Mechanics*, *87*(2-3), 283–305.

Gamage, P. K., Brien, M. O., & Karunanayake, L. (2009). Epoxidation of some vegetable oils and their hydrolysed products with peroxyformic acid - optimised to industrial scale, *37*(4), 229–240.

García-Pacios, V., Colera, M., Iwata, Y., & Martín-Martínez, J. M. (2013). Incidence of the polyol nature in waterborne polyurethane dispersions on their performance as coatings on stainless steel. *Progress in Organic Coatings*, *76*(12), 1726–1729.

García-Pacios, V., Costa, V., Colera, M., & Martín-Martínez, J. M. (2011). Waterborne polyurethane dispersions obtained with polycarbonate of hexanediol intended for use as coatings. *Progress in Organic Coatings*, *71*(2), 136–146.

García-Pacios, V., Costa, V., Colera, M., & Miguel Martín-Martínez, J. (2010). Affect of polydispersity on the properties of waterborne polyurethane dispersions based on polycarbonate polyol. *International Journal of Adhesion and Adhesives*, *30*(6), 456–465.

Garrison, T. F. (2013). *Synthesis and characterization of vegetable oil- based polyurethane dispersions* (Doctoral dissertation). Iowa State University, Ames, Iowa). Paper 13470

Garrison, T. F., Kessler, M. R., & Larock, R. C. (2014). Effects of unsaturation and different ring-opening methods on the properties of vegetable oil-based polyurethane coatings. *Polymer (United Kingdom)*, *55*, 1004–1011.

Gite, V. V., Chaudhari, A. B., Kulkarni, R. D., & Hundiwale, D. G. (2013a). Renewable source-based polyurethane coatings by using monoglycerides of vegetable oils and its modification by nano TiO. *Pigment & Resin Technology*, *42*, 353–361.

Gite, V. V., Chaudhari, A. B., Kulkarni, R. D., & Hundiwale, D. G. (2013b). Renewable source-based polyurethane coatings by using monoglycerides of vegetable oils and its modification by nano TiO2. *Pigment & Resin Technology*, *42*(6), 353–361.

Goud, V. V., Dinda, S., Patwardhan, A. V., & Pradhan, N. C. (2010). Epoxidation of Jatropha (Jatropha curcas) oil by peroxyacids. *Asia-Pacific Journal of Chemical Engineering*, 346–354.

Goud, V. V., Patwardhan, A. V., Dinda, S., & Pradhan, N. C. (2007). Kinetics of epoxidation of jatropha oil with peroxyacetic and peroxyformic acid catalysed by acidic ion exchange resin. *Chemical Engineering Science*, *62*(15), 4065–4076.

GreenOdin. (2015). GreenOdin Global Ltd. Retrieved November 16, 2015, from http://greenodin.com/products/go-biodiesel/go-biomass-feedstock/jatropha/

Guo, A., Cho, Y., & Petrović, Z. S. (2000a). Structure and properties of halogenated and nonhalogenated soy-based polyols. *Journal of Polymer Science, Part A: Polymer Chemistry*, *38*(21), 3900–3910.

Guo, A., Cho, Y., & Petrović, Z. S. (2000b). Structure and properties of halogenated and nonhalogenated soy-based polyols. *Journal of Polymer Science, Part A: Polymer Chemistry*, *38*(21), 3900–3910.

Guo, A., Demydov, D., Zhang, W., & Petrovic, Z. S. (2002). Polyols and polyurethanes from hydroformylation of soybean oil. *Journal of Polymers and the Environment*, *10*(1-2), 49–52.

Harjono, Sugita, P., & Alim Mas'ud, Z. (2012). Synthesis and Application of Jatropha Oil based Polyurethane as Paint Coating Material. *Makara Journal of Science*, *16/2*, 134–140.

Hazmi, A. S. A., Aung, M. M., Abdullah, L. C., Salleh, M. Z., & Mahmood, M. H. (2013). Producing Jatropha oil-based polyol via epoxidation and ring opening. *Industrial Crops and Products*, *50*, 563–567. doi:10.1016/j.indcrop.2013.08.003

Hwang, H.-D., Park, C.-H., Moon, J.-I., Kim, H.-J., & Masubuchi, T. (2011). UV-curing behavior and physical properties of waterborne UV-curable polycarbonate-based polyurethane dispersion. *Progress in Organic Coatings*, *72*(4), 663–675.

Ionescu, M. (2005). *Chemistry and Technology of Polyols for Polyurethanes*. UK: Rapra Technology Limited.

Kamsons Chemicals Pvt. Ltd. (n.d.). Kamthane-1432. Retrieved November 3, 2015, from http://www.kamsons.com/k-1432.html

Kastner, U. (2001). The impact of rheological modifiers on water-borne coatings. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *183-185*, 805–821.

Kong, X., Liu, G., Qi, H., & Curtis, J. M. (2013). Preparation and characterization of high-solid polyurethane coating systems based on vegetable oil derived polyols. *Progress in Organic Coatings*, *76*(9), 1151–1160.

Kong, X., & Narine, S. S. (2007). Physical properties of polyurethane plastic sheets produced from polyols from canola oil. *Biomacromolecules*, *8*(7), 2203–9.

Krevelen, D. W. van, & Nijenhuis, K. te. (2009). *Properties of Polymers* (fourth, co.). Amsterdam: Elsevier B.V.

Kumar, A., & Sharma, S. (2008). An evaluation of multipurpose oil seed crop for industrial uses (Jatropha curcas L.): A review. *Industrial Crops and Products*, *28*(1), 1–10.

Kwak, Y. S., & Kim, H. Do. (2002). Preparation and Properties of Waterborne Polyurethanes Based on Triblock Effect of Soft Segment Content, *3*(4), 153–158.

Lee, J. S., & Kim, B. K. (1995). Poly(urethane) cationomers from poly(propylene) glycol and isophorone diisocyanate: emulsion characteristics and tensile properties of cast films. *Progress in Organic Coatings*, *25*(4), 311–318.

Lei, L., Xia, Z., Cao, G., & Zhong, L. (2013). Synthesis and adhesion property of waterborne polyurethanes with different ionic group contents. *Colloid and Polymer Science*, *292*(2), 527–532.

Li, S., Vatanparast, R., & Lemmetyinen, H. (2000). Cross-linking kinetics and swelling behaviour of aliphatic polyurethane. *Polymer*, *41*(15), 5571–5576.

Lligadas, G., Ronda, J. C., Galià, M., & Cádiz, V. (2010). Plant Oils as Platform Chemicals for Polyurethane Synthesis: Current State-of-the-Art. *Biomacromolecules*, 2825–2835.

Lu, Y., & Larock, R. C. (2008). Soybean-oil-based waterborne polyurethane dispersions: effects of polyol functionality and hard segment content on properties. *Biomacromolecules*, *9*(11), 3332–40. doi:10.1021/bm801030g

Madbouly, S. a., Otaigbe, J. U., Nanda, A. K., & Wicks, D. a. (2005a). Rheological Behavior of Aqueous Polyurethane Dispersions: Effects of Solid Content, Degree of Neutralization, Chain Extension, and Temperature. *Macromolecules*, *38*(9), 4014–4023.

Madbouly, S. a., Otaigbe, J. U., Nanda, A. K., & Wicks, D. a. (2005b). Thermal-induced simultaneous liquid–liquid phase separation and liquid–solid transition in aqueous polyurethane dispersions. *Polymer*, *46*(24), 10897–10907.

Madbouly, S. a., Xia, Y., & Kessler, M. R. (2013). Rheological behavior of environmentally friendly castor oil-based waterborne polyurethane dispersions. *Macromolecules*, *46*(11), 4606–4616.

Mahendran, A. R., Wuzella, G., Aust, N., Kandelbauer, A., & Müller, U. (2012). Photocrosslinkable modified vegetable oil based resin for wood surface coating application. *Progress in Organic Coatings*, *74*, 697–704.

Manion, S. J., Johnson, L. L., & Fernando, R. H. (2011). Shear-thickening in aqueous surfactant-associative thickener mixtures. *Journal of Coatings Technology and Research*, *8*(3), 299–309.

Meier, M. a R., Metzger, J. O., & Schubert, U. S. (2007). Plant oil renewable resources as green alternatives in polymer science. *Chemical Society Reviews*, *36*, 1788–1802.

Melchiors, M., Sonntag, M., Kobusch, C., & Jürgens, E. (2000). Recent developments in aqueous two-component polyurethane (2K-PUR) coatings. *Progress in Organic Coatings*, *40*(1-4), 99–109.

Meyer, P., Techaphattana, N., Manundawee, S., & Sangkeaw, S. (2008). Epoxidation of Soybean Oil and Jatropha Oil. *Thammasat Int. J. Sc. Tech.*, *13*(November), 1–5.

Miao, S., Wang, P., Su, Z., & Zhang, S. (2014). Vegetable-oil-based polymers as future polymeric biomaterials. *Acta Biomaterialia*, *10*(4), 1692–1704.

Mielke, T. (2014). Global supply, demand and prices outlook of oil and fats, impacts on palm oil. *Malaysian Oil and Science Technology*, *23*(1), 13–27.

Mofijur, M., Masjuki, H. H., Kalam, M. a., Hazrat, M. a., Liaquat, a. M., Shahabuddin, M., & Varman, M. (2012). Prospects of biodiesel from Jatropha in Malaysia. *Renewable and Sustainable Energy Reviews*, *16*(7), 5007–5020.

Nanda, A. K., & Wicks, D. a. (2006). The influence of the ionic concentration, concentration of the polymer, degree of neutralization and chain extension on aqueous polyurethane dispersions prepared by the acetone process. *Polymer*, *47*(6), 1805–1811.

Narine, S. S., Kong, X., Bouzidi, L., & Sporns, P. (2006). Physical Properties of Polyurethanes Produced from Polyols from Seed Oils: I. Elastomers. *Journal of the American Oil Chemists' Society*, *84*(1), 55–63.

Negim, E.-S. M., Bekbayeva, L., Grigory A., M., Abilov, Z. A., & Saleh, M. I. (2011). Effects of NCO/OH Ratios on Physico-Mechanical Properties of Polyurethane Dispersion. *World Applied Sciences Journal*, *14*(3), 402–407.

Ni, B., Yang, L., Wang, C., Wang, L., & Finlow, D. E. (2010). Synthesis and thermal properties of soybean oil-based waterborne polyurethane coatings. *Journal of Thermal Analysis and Calorimetry*, *100*(1), 239–246.

Nielson, L. E., & Landel, R. F. (1994). *Mechanical Properties of Polymers and Composites* (Second edi.). Marcel Dekker Inc.

Nieto, E. del R. (2011). *New polyurethanes from vegetable oil-based polyols*. Universitat Rovira I Virgili.

Noble, K.-L. (1997). Waterborne polyurethanes. *Progress in Organic Coatings*, *32*(1-4), 131–136.

Patel, A., Patel, C., Patel, M. G., Patel, M., & Dighe, A. (2010a). Fatty acid modified polyurethane dispersion for surface coatings: Effect of fatty acid content and ionic content. *Progress in Organic Coatings*, *67*(3), 255–263.

Patel, A., Patel, C., Patel, M. G., Patel, M., & Dighe, A. (2010b). Fatty acid modified polyurethane dispersion for surface coatings: Effect of fatty acid content and ionic content. *Progress in Organic Coatings*, *67*(3), 255–263.

Patel, V. C., Varughese, J., Krishnamoorthy, P. A., Jain, R. C., Singh, A. K., & Ramamoorty, M. (2008). Synthesis of Alkyd Resin from Jatropha and Rapeseed Oils and Their Applications in Electrical Insulation. *Journal of Applied Polymer Science*, *107*, 1724–1729.

Pathak, S. S., Sharma, a., & Khanna, a. S. (2009). Value addition to waterborne polyurethane resin by silicone modification for developing high performance coating on aluminum alloy. *Progress in Organic Coatings*, *65*(2), 206–216.

Peng, S., Jin, Y., Sun, T., Qi, R., Fan, B., & Cheng, X. (2014). Synthesis of high solid content waterborne polyurethanes with controllable bimodal particle size distribution. *Journal of Applied Polymer Science*, *131*(12), n/a–n/a.

Peng, S.-J., Jin, Y., Cheng, X.-F., Sun, T.-B., Qi, R., & Fan, B.-Z. (2015). A new method to synthesize high solid content waterborne polyurethanes by strict control of bimodal particle size distribution. *Progress in Organic Coatings*, *86*, 1–10.

Petrovic, Z. (2008). Polyurethanes from Vegetable Oils. *Polymer Reviews*, *48*(1), 109–155.

Petrovic, Z., Javni, I., Guo, A., & Zhang. (2004). Method of Making Natural Oil-based Polyols and Polyurethane Therefrom.

Petrovic, Z. S. (2010). POLYMERS FROM BIOLOGICAL OILS. *Contemporary Materials*, *1*, 39–50.

Petrović, Z. S., & Ferguson, J. (1991). *Polyurethane elastomers*. *Progress in Polymer Science* (Vol. 16).

Petrović, Z. S., Zhang, W., & Javni, I. (2005). Structure and properties of polyurethanes prepared from triglyceride polyols by ozonolysis. *Biomacromolecules*, *6*(2), 713–719.

Petrovic, Z. S., Zlatanic, A., Lava, C. C., & Sinadinovic-Fiser, S. (2002). Epoxidation of soybean oil in toluene with peroxoacetic and peroxoformic acids – kinetics and side reactions Research Paper. *European Journal of Lipid Science and Technology*, *104*, 293–299.

Philipp, C., & Eschig, S. (2012). Waterborne polyurethane wood coatings based on rapeseed fatty acid methyl esters. *Progress in Organic Coatings*, *74*(4), 705–711.

Rios, L. a., Echeverri, D. a., & 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.

Ristić, I., Cakić, S., Ilić, O., Budinski-Simendić, J., & Marinović-Cincović, M. (2012). Investigation of Potentional Use of Recycled Poly(Ethylene Terephthalate) in Polyurethane Synthesis. *Contemporary Materials*, *1*(3).

Rozman, H. D., Tai, N. L., & Tay, G. S. (2013). Ultra-violet curable resin based on palm oil: Determination of reaction condition and characterization of the resin. *Journal of Applied Polymer Science*, *127*(4), 3040–3046.

Salimon, J., & Ahmed, W. (2012). Physicochemical Characteristics of Tropical Jatropha curcas Seed Oil. *Sains Malaysiana*, *41*(3), 313–317.

Salleh, M. Z., Badri1, K. H., Mahmood, M. H., & Ahmad, S. H. (2010). Synthesis of UV-curable hyperbranched urethane acrylate from palm oil oleic acid. *Journal of Nuclear and Related Technologies*, *7*(2), 38–48.

Samarth, N. B., & Mahanwar, P. A. (2015). Modified Vegetable Oil Based Additives as a Future Polymeric Material — Review. *Open Journal of Organic Polymer Materials*, *5*, 1–22.

Saravari, O., & Praditvatanakit, S. (2013). Preparation and properties of urethane alkyd based on a castor oil / jatropha oil mixture. *Progress in Organic Coatings*, *76*, 698–704.

Sarin, R., Sharma, M., Sinharay, S., & Malhotra, R. K. (2007). Jatropha–Palm biodiesel blends: An optimum mix for Asia. *Fuel*, *86*(10-11), 1365–1371.

Saurabh, T., Patnaik, M., Bhagt, S. L., & Renge, V. C. (2011). Epoxidation of vegetable oils: A review. *International Journal of Advanced Engineering Technology*, *II*(Iv), 491–501.

Scrinzi, E., Rossi, S., Deflorian, F., & Zanella, C. (2011). Evaluation of aesthetic durability of waterborne polyurethane coatings applied on wood for interior applications. *Progress in Organic Coatings*, *72*(1-2), 81–87.

Sefcik, J., Grass, R., Sandkühler, P., & Morbidelli, M. (2005). Kinetics of Aggregation and Gelation in Colloidal Dispersions. *Chemical Engineering Research and Design*, *83*(7), 926–932.

Seniha Güner, F., Yağci, Y., & Tuncer Erciyes, a. (2006). Polymers from triglyceride oils. *Progress in Polymer Science (Oxford)*, *31*(7), 633–670.

Shaw, M. T. (2012). *Introduction to Polymer Rheology*. Hoboken, New Jersey: John Wiley & Sons, Inc.

Sow, C., Riedl, B., & Blanchet, P. (2010). UV-waterborne polyurethane-acrylate nanocomposite coatings containing alumina and silica nanoparticles for wood: mechanical, optical, and thermal properties assessment. *Journal of Coatings Technology and Research*, *8*(2), 211–221.

Tan, S. G., & Chow, W. S. (2010). Biobased Epoxidized Vegetable Oils and Its Greener Epoxy Blends: A Review. *Polymer-Plastics Technology and Engineering*, *49*(15), 1581–1590.

Tan, S. G., & Chow, W. S. (2011). Thermal properties, curing characteristics and water absorption of soybean oil-based thermoset. *Express Polymer Letters*, *5*(6), 480–492.

Tawa, T., & Ito, S. (2006). The Role of Hard Segments of Aqueous Polyurethane-urea Dispersion in Determining the Colloidal Characteristics and Physical Properties. *Polymer Journal*, *38*(7), 686–693.

Tent, A., Zohrehvand, S., & Nijenhuis, K. (2013). Characterization of film formation in waterborne polymer lattices: a focus on turbidimetry. *Journal of Coatings Technology and Research*, *11*(2), 159–167.

Tielemans, M., Roose, P., Groote, P. De, & Vanovervelt, J.-C. (2006a). Colloidal stability of surfactant-free radiation curable polyurethane dispersions. *Progress in Organic Coatings*, *55*(2), 128–136.

Tielemans, M., Roose, P., Groote, P. De, & Vanovervelt, J.-C. (2006b). Colloidal stability of surfactant-free radiation curable polyurethane dispersions. *Progress in Organic Coatings*, *55*(2), 128–136.

Transparency Market Research. (2015a). Despite volatile raw materials prices, polyols and polyurethane market poised to exhibit steady growth till 2023. Retrieved May 10,2016,from http://www.transparencymarketresearch.com/pressrelease/polyols-market.htm

Transparency Market Research. (2015b). The Global Polyurethane Dispersions Market to Grow at 7.5% CAGR between 2012 and 2018. Retrieved August 31, 2015,from http://www.transparencymarketresearch.com/pressrelease/polyurethane-dispersions-market.htm

Wan Rosli, W. D., Kumar, R. N., Mek Zah, S., & Hilmi, M. 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.

Wan, X., Petrovic, Z. S., Upshaw, T. A., Ionescu, M., & Radojc, D. (2015). Functionalized vegetable oils as precursors for polymers by thiol-ene reaction, 1–10.

Wang, R. (2014). *Manufacturing of vegetable oils-based epoxy and composites for structural applications*. Missouri University of Science and Technology.

Wool, R. P. (2005). Pressure-Sensitive Adhesives, Elastomers, and Coatings from Plant Oil. In *Bio-based Polymers and Composites* (pp. 256–291).

Xia, Y., & Larock, R. C. (2010). Vegetable oil-based polymeric materials: synthesis, properties, and applications. *Green Chemistry*, *12*(11), 1893–1909.

Xia, Y., & Larock, R. C. (2011). Castor-Oil-Based Waterborne Polyurethane Dispersions Cured with an Aziridine-Based Crosslinker. *Macromolecular Materials and Engineering*, *296*(8), 703–709.

Xu, H., Qiu, F., Wang, Y., Wu, W., Yang, D., & Guo, Q. (2012). UV-curable waterborne polyurethane-acrylate: preparation, characterization and properties. *Progress in Organic Coatings*, *73*(1), 47–53.

Xu, Y., Petrovic, Z., Das, S., & Wilkes, G. L. (2008). Morphology and properties of thermoplastic polyurethanes with dangling chains in ricinoleate-based soft segments. *Polymer*, *49*(19), 4248–4258.

Yoon Jang, J., Kuk Jhon, Y., Woo Cheong, I., & Hyun Kim, J. (2002). Effect of process variables on molecular weight and mechanical properties of water-based polyurethane dispersion. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *196*(2-3), 135–143.

Zhang, J., Tang, J. J., & Zhang, J. X. (2015). Polyols Prepared from Ring-Opening Epoxidized Soybean Oil by a Castor Oil-Based Fatty Diol. *International Journal of Polymer Science*, *2015*, 1–8.

Zhang, J., Tu, W., & Dai, Z. (2012). Synthesis and characterization of transparent and high impact resistance polyurethane coatings based on polyester polyols and isocyanate trimers. *Progress in Organic Coatings*, *75*(4), 579–583.

Zlatanic, A., Lava, C., Zhang, W., & Petrović, Z. S. (2004). Effect of Structure on Properties of Polyols and Polyurethanes Based on Different Vegetable Oils. *Journal of Polymer Science: Part B: Polymer Physics*, *42*, 809–819.