Title of the Research

Development of castor oil based bio-binder for composite materials

MSc RESEARCH DISSERTATION

Prepared by

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Submitted to

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Declaration

I hereby declare that this MSc Dissertation entitled "***Development of castor oil based bio-binder for composite materials***" was carried out by me.

The content and discussions put forth are based on my reading and understanding of the published documentations, and this report was not submitted for any degree or diploma before, either in this or in any other University. All documentation used are acknowledged at the respective place in the text.

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Abstract

The development of polymer based products in various industries has decreased as a result of depleting fossil fuels and increasing environmental concerns such as greenhouse gases, global warming and population. However, vegetable oils have emerged as a worthy replacement for fossil fuels. The need to use non-edible oils is recommended for industrial processes to reduce the dependency on edible oils and hence increasing food security. The main objective of this investigation is to use an affordable process to develop bio-binders for composite materials by using non-edible oil produced from castor seed.

The extraction of oil from the castor seeds was done using the Soxhlet extraction set-up. After purification, the processed to yield castor oil-based bio-binders was done through Polycondensation, Epoxidation and Ozonolysis methods. Polycondensation is a three step process. The first step is the synthesis of the N, N-Bis (2-hydroxyethyl) Castor Oil Fatty Amide (HECA), followed by the synthesis of the Castor Oil Polyesteramide (CPEA) and lastly, the synthesis of Castor Oil Polyurethane - esteramide (UCPEA). The polycondensation process was monitored by Thin Layer Chromatography (TLC) until the production of the polyurethane, and temperatures range was 120 – 250 °C at various stages of the process. The polyurethane peak was observed at 1618 cm^{-1} and 1459 cm^{-1} using Fourier-transform infrared spectroscopy (FTIR).

Ozonolysis was a two-step process whereby firstly it was the synthesis of the polyols by converting the vinyl group to an ozo-group by using ozone at very low temperatures (-30 to -40 °C). This was followed by the second step which is the synthesis of the polyurethanes from the polyols (70 – 110 °C). The ozo (c-o) peak was observed using FTIR at 1269 and 875 cm^{-1}.

The Epoxidation catalyst was synthesized from of tungstic acid and hydrogen peroxide between 50 - 60 °C. The Epoxidation process temperature varied between 60 and 100 °C while varying the catalyst loading and the reaction time. The epoxy peak was also observed using FTIR at 830 cm^{-1}.

Additional characterizations that were done for the three processes include thermal stability using and rheology properties. The effect of castor oil content on the epoxidation and ozonolysis process showed that 5 % oil excess is sufficient to prepare a castor oil based binder.

From the results obtained, ozonolysis was a better process as compared to polycondensation and epoxidation. Based on the yield processed and it is also recommended from those investigation of ozonolysis as this process uses the least amount of temperature, reagents and processing steps making the process more energy. However, it is recommended that more investigations be done in order to confirm the findings.

Acknowledgement

This study would have been impossible to complete without the financial support of the Department of science and technology, CSIR and the University of the Witwatersrand. I would like to thank the University of the Witwatersrand for affording me an opportunity to complete my studies with the institution. In particular, I am indebted to my supervisor, Dr D Nkazi and co-supervisor; Dr H Mukaya, who have been supportive of my academic career goals and who worked enthusiastically to afford me guidance and time to pursue my academic goals, and thank you for all your prayers.

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My dearest Husband, Rhulani Khosa, you have been a pillar and firm supporter of my goals. My deepest gratitude for all the financial, emotional, and spiritual support. You have always prayed and encouraged me to pursue my dreams and I am glad that you have supported me to achieve this goal.

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%	Percentage
% W/W	weight per weight percentage
°C	Degrees Celsius
CH_3COOH	Acetic acid
CHT	Catalytic transfer hydrogenation
CO	Castor oil
cP	Centipoise
CPEA	Castor Oil Polyesteramide
CSIR	Council for Scientific and Industrial Research
DMBA	dimethylol butyric acid
FTIR	Fourier- transform infrared spectroscopy
g/cm^3	gram per cubic meter
GPa	Gigapascal
H	Hour
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulfuric Acid
H_3PO_4	Orthophosphoric acid
HECA	N, N-Bis (2-hydroxyethyl) Castor Oil Fatty Amide
HHV	Higher heating value
Kg/m^3	kilogram per cubic meter
KOH	Potassium hydroxide
MDI	Methylene diphenyl diisocyanate
ml	Milliliters
mm^2/s	square millimeter per second

Mn	Formula Weight
MPa	Mega Pascal
N_2	Nitrogen gas
Na_2SO_4	Sodium sulphate
$NaBH_4$	Sodium borohydride
NaCl	Sodium Chloride
NMR	Nuclear magnetic resonance Spectroscopy
O_3	Ozone
PTMEG	Polytetramethylene ether glycol
SSD	Sediba sa Dimelana
TDI	toluene-2-4-diisocyanate
TEA triethylamine	triethylamine
TGA	Thermogravimetric analysis
Ti(IV)	Titanium(four)
TLC	thin layer chromatography
UCPEA	Castor Oil Polyurethane – esteramide

Chapter 1. Background and Motivation

The world is currently discussing matters around global warming, the effect of greenhouse gases, significant increase in population, depletion of natural resources and the demanded expansion of urban infrastructure; hence there is a great need to be innovative and come up with technologies that are environmentally friendly and can be regenerated. These technologies will include the substitution of petroleum with natural oils from plants (Gondim et al., 2016).

The use of natural oils from different plants such as vegetables has gained research popularity over the years due to the fact that they have renewable properties and are environmentally friendly. The different types of natural oils such as castor oil, olive oil, soybean oil, linseed oil, etc.; are used in various industries such as paints, cosmetics, coats and lubricants (Shaik et al., 2015). Most technologies are concentrating on the use of castor oil because it is regarded as a low cost renewable resource; therefore this then allows for research in the application of vegetable oils for the production of polymers that contain sufficient physiochemical properties for different applications (Nayak, 1998).

Most polymers such as polyurethane, epoxy, polyesteramide, and polyetheraminde are produced from vegetable oils. Research has shown that these polymers are considered to be biodegradable, less volatile, non-toxic, easy to modify, and the oils can be obtained in large quantities. These polymers are used for different applications such as binders and in different industries such as the automotive industry.

The depletion of fossil fuel and the increasing demand of polymeric materials such as binders have directed current research into renewable resources as primary materials for the development of polymeric materials. There is a demand from industry for cheaper, safer and renewable resources that can be used for the development of polymeric materials. It is therefore imperative that the further developmental work should be done to develop bio-binders for composite materials from non-edible vegetable oils such as castor oil.

1.1. Problem statement

South Africa has over the years increased its demand in the need of non-edible oils for various production of polymers. With the challenges faced over the use of petroleum for the development of polymers, South Africa has found itself importing more non-edible oil; such as Jatropha, karanja and castor oils; due to high demands (Chisoro-Dube et al., 2018). There are currently not enough agri-enterprenuers in South Africa who are producing non-edible oil such as castor oil, therefore the high importation of the oil. The development of automotive and aviation industries requires the use of composite materials for automotive and aviation bodies. Currently raw materials for binders used for composite materials are fossil fuel and edible oil. The use of seeds with higher oil content can reduce the challenge with green house effects and production costs of the bio-binder production process.

1.2. Research Aim and Objectives

The depletion of fossil fuel and the increasing demand of polymeric materials such as binders has directed current research into renewable resources as primary materials for the development of polymer-based materials. The question then remains if castor oil can be used as a renewable source for polymer development, especially bio-binders for composite materials.

The main aim of this research was to identify and compare three selected methods to develop a bio-binder production process from locally produced castor-oil, and this will be achieved through the following objectives:

a. Modification of castor oil functional groups to introduce bio-binder properties;

b. Polymerization of the modified castor oil as a monomer;

c. Optimize the three selected methods (Polycondensation, epoxidation and ozonolysis) for bio-binder development

Chapter 2. Literature Review

The current production processes have brought about concerns in the petroleum industry. These concerns are related to the mining and processing of crude oil and these include the results due to climate change, increased population, increased pollution and the decrease of natural resources. As an effect of the concerns, engineers and scientists have started researching on other techniques to implement the use of natural resources with required traits for applications of various industries (Gokdogan et al., 2015) such as paints, cosmetics, and lubricants (Shaik et al., 2015).

Various oils are being used in production processes with the focus shifting towards non-edible oils such as castor oil. Castor oil is a cheaper renewable resource and most importantly, castor oil has an advantage over oils such as olive oil because it does not threaten people's livelihood and food source. Therefore this then allowed the production processes of polymers to use vegetable oils because they contain good physicochemical properties for different applications (Nayak , 2000).

Application of bio-based polymers was the initial technology applied using bio-oils as biodegradable and renewable resources. Ober the years, petroleum gained more popularity due to the increased use and production of synthetic polymers. However, due to increasing demand, because rapid growth in the global population has increased the need for the production of synthetic polymers and the decrease in supply of fossil fuels and thus returning to the initial use of plant oils as a renewable resource (Dotan, 2014).

There are various polymers that are produced from natural oils, for example polyurethane, epoxy, polyesteramide, and polyetheraminde. Research has shown that these polymers are considered to be biodegradable, less volatile, non-toxic, easy to modify, and the oils can be obtained in large quantities. These polymers are used for different applications such as binders and in different industries such as the automotive industry (Suhane et al., 2012), civil

engineering (Attia et al., 2017; Forth & Zoorob, 2008) and the coatings industry (Alam et al., 2014).

2.1. The origin of castor oil

Castor oil is derived from the seeds of a castor plant, also known as *Ricinus communis*, which is from the Euphorbiaceae family. The castor seeds usually contain up to 50% of the castor oil (Mubofu, 2016). The seeds grow at different rates and therefore makes the plant non-determinant, hence resulting in difficulties while harvesting. The plant also grows in rather difficult environments and thus contributes to harvesting challenges. The other challenge is that the seed produces lipids with toxic ricin that can be considered to be an allergen, therefore making the everyday harvesting process a challenge and poisonous to harvesters. However, the composition of fatty acids in castor oil makes it worthwhile to harvest (Stohr, 2015).

Figure 1 illustrates the composition of castor oil fatty acid whereby the makeup of the castor oil has the ricinoleic acid dominating with approximately ± 90 % of the castor oil. The rest of the acidic structures make up the remaining ± 10 % of the structure. This therefore means that the best way to modify the castor oil would be to target the ricinoleic acid in order to maximise the synthesis output.

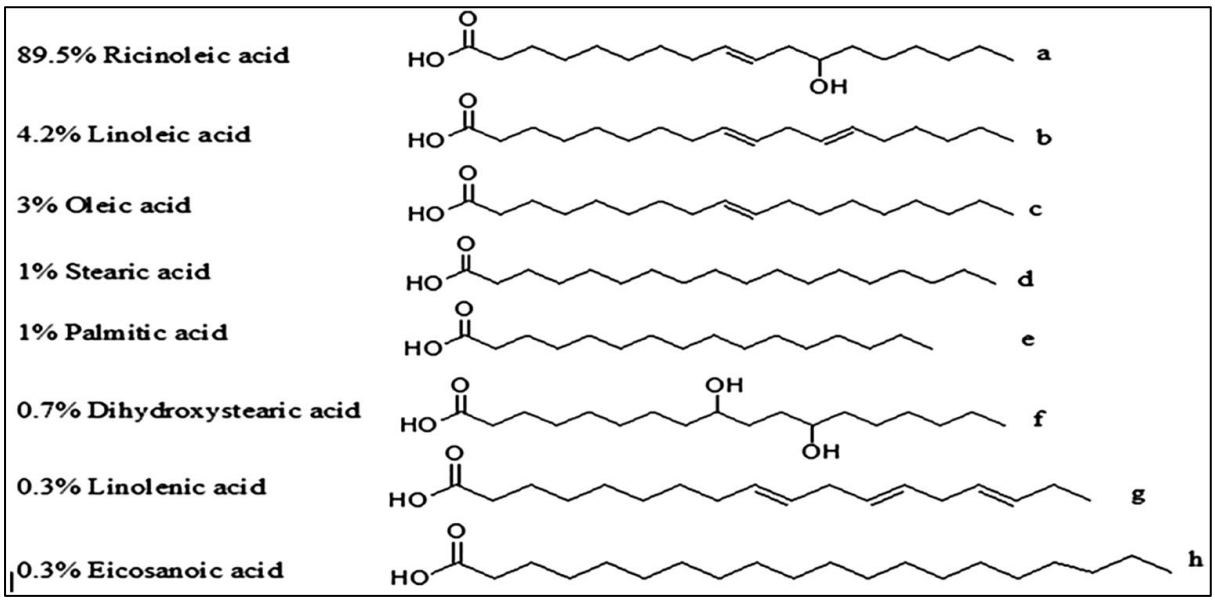

Figure 1: Amounts of fatty acids in castor oil (Mubofu, 2016)**.**

2.2. Overview of the castor oil industry

In the past, agricultural resources like bio-oils were predominantly applied in food production processes; on the other hand, their requirement for implementation in other industrial sectors amplified (Derksen et al., 1996). Because of the great need of bio-degradable resources, particularly the resources industry from the United States of America, India, and Brazil; India has been found to be the biggest contributor to this industry and the trend has been seen to increase over the years. From 2003 to 2013 as seen in Figure 2, the study of the global castor oil market illustrates that there could be an increase beyond 1.8 billion dollars by 2020 (Mubofu, 2016).

The use of biofuels has shown growth over the past two decades and hence has been of interest in the current research and new technology development. Currently, there is an increase in the bio-based economy as an alternative to the fossil fuel–based economy. Biofuels are used because they are renewable, cheap, and environmentally friendly and they come in two phases, that is, liquid and gas (Raouf et al., 2010). The price of crude oil has increased significantly in the past decade, that is, from US$150/ 1000 tons to US$1000/1000 tons, hence increasing the demand to replace crude oil with vegetable oils such as castor oil. Annual production of castor oil is 271 million tons (Chauhan & Chhibber, 2013) and it is obtained in a pale colour in the market and contains the properties that are outlined in Table 1.

The oil yields (tons/ha/year) and castor seeds give the lowest yield of oil as compared to the other seeds as shown in Table 1 (Banković-Ilić et al., 2012; Kumar & Sharma, 2015), It can be seen that castor seeds are the highest each year and with a great amounts of oil (Asadauskas, et al., 1996). This is a result of the harvesting challenges of castor seeds, for example, it is much easier to harvest Jatropha seeds as compared to castor seeds because they are not as much toxic while harvesting and therefore more Jatraopha seeds are harvested as compared to castor seeds (Gokdogan et al., 2015).

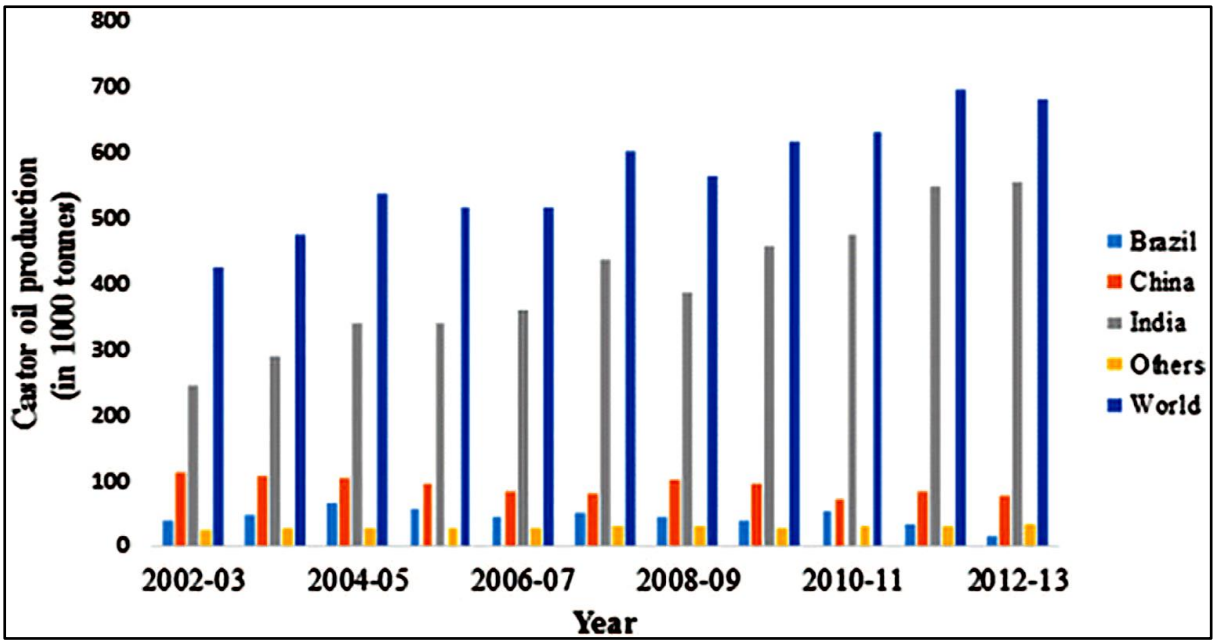

Figure 2: Amounts of castor oil production from by major producing countries (2002–2013) (Mubofu, 2016)

Table 1: Amounts of Non-Edible Oil Seeds and oil contents produced. (Suhane et al., 2012; Banković-Ilić et al., 2012; Kumar & Sharma, 2015)

Non-edible oil seeds	Oil content (%)	Seed estimate (10^6 Tonnes/year	Oil yield (Tonnes/ Ha/ year)
Castor	45 - 50	0.25	0.50 - 1.00
Jatropha	50 – 60	0.20	2.00 - 3.00
Karanja	30 - 40	0.06	2.00 - 4.00
Mahau	35 – 40	0.20	1.00 - 4.00
Neem	23 – 30	0.10	2.00 - 3.00

Table 2: Chemical and physical Properties of Non-Edible Oils (Suhane et al., 2012; Banković-Ilić et al., 2012; Karmakar et al., 2010)

Vegetable oils	Density (Kg/m^3)	Kinematic Viscosity ((40°C), mm^2/s)	Oxidation Stability (110°C, h)	Cloud Point (°C)	Flash Point (°C)
Castor	899	15.25	1.1	-13.4	260
Jatropha	880	4.8	2.3	2.7	135
Karanja	920	4.8	6	9	150
Mahau	850	3.98	-	-	208
Neem	884	5.21	7.1	14.4	42

Table 2 illustrates the chemical and physical properties of comparative non-edible vegetable oils that are applied in the lubricant industry (Suhane et al., 2012; Karmakar et al., 2010). There are comparisons in the densities of the oils, with castor oil having a density of 899 kg/m^3. However, castor oil can be different from the other oils based on viscosity, oxidation stability, cloud point, and flash point. Castor oil has the highest viscosity of 15.25 (40°C, $mm^2\ s^{-1}$), meaning that it is thicker than the other oils and therefore does not easily flows and therefore can withstand high temperatures (Diamante & Lan, 2014).

Castor oil has the lowest oxidative stability (1.1 at 110°C, h), and the lower oxidative stability is obtained due to double bonds and hydroxyl functional groups that are present because they are likely to be broken into single bonds, therefore resulting in the formation of volatiles. The low oxidative stability is also due to the high fatty acid content; the more acidic the oil is, the more it is prone to oxidation (Ali et al., 2016). Castor oil also has a very low cloud point, meaning that there is no presence of solidified waxes that thickens the oil and clog filters, pumps, and/or injectors in processing plants. The low cloud point also makes the castor oil suitable to be used in very cold environments for applications such as biodiesel (Forero, 2005). And the highest flash point of castor oil means that the oil is not prone to ignition (less

flammable) as compared to the others (Patel et al., 2016), therefore, being safer to handle or transport at temperatures below 260°C.

The vegetable oil plants in Table 2 can be grown and established in marginal and semi-marginal land under varied agro-climatic conditions. Therefore, edible oilseed usage for fuel and lubricant needs may not be able to meet the domestic requirements of the ever increasing population unless more tropical environments get involved in the agriculture of farming vegetable oils. As an alternative, non-edible vegetable oil can prove to be worthwhile due to the depletion of fossil fuels and increasing populations (Suhane et al., 2012; Dresel & Mang, 2007).

Bio-oils are obtained from both plants and animals, such as vegetables, plants (algae), and fish and Table 3 compares that properties of two plant oils. Plant oils, which are of interest to us, are considered to be lipids which contain both hydrophilic and lipophilic functional groups. The oil is a mixture of different types of triacylglycerol (or triglycerides) (Dotan, 2014). The various applications have led to the new emerging markets that are looking at biopolymers such as polyurethanes and polyethylene (Bergstra, 2007). The other reason for increasing interest in biofuels is that lignin-containing by-products are obtained in biofuel production plants, therefore leading to various applications as well (Raouf et al., 2010). The plant history and the chemistry of castor oil enable the research into bio-binders and polymers to vary for different applications.

Table 3: Properties of bio-oils (Mohammed et al., 2014; Şensöz et al., 2000).

Properties	**Bio-oil**	
Ultimate analysis (W/W %)	Castor seed	Rapeseed
Carbon	74.5	52.25
Hydrogen	10.76	8.06
Nitrogen	2.56	3.91
Oxygen	11.78	35.78

H/C molar ratio	1.76	1.85
O/C molar ratio	0.12	0.51
Calorific value MJ/kg	35.01	28.36
Empirical formula	$CH_{1.7}CO_{0.15}N_{0.03}$	$CH_{1.85}O_{0.51}N_{0.06}$

2.3. Castor oil–based chemical processes

2.3.1. Fatty acid composition of castor oil

Castor oils contain both a hydroxyl group and an olefinic link (El-Adly & Shoaib, 2014). The ricinoleic acid forms approximately 90% as seen in Figure 1 of the total fatty acid content in castor oil (Stohr, 2015) and the rest accounts for 10%. The ricinoleic structure contains most of the chemical and physical properties of castor oil as shown in Figure 1 (Mubofu, 2016). The hydroxyl group enhances the physical and chemical properties of castor oil. The physical properties are higher viscosity and higher solubility in most solvents (Gilbert, 1941). The chemistry of castor oils allow the modification of its different functional groups such as the hydroxyl group, vinyl group, and the ester group.

Castor oil does not show any drying properties; however, it is still of interest in coating industries because it is stable (Tadesse, 2015). It is available commercially in the form of natural hydroxylated triglycerides. The hydroxyl group that is contained in triglycerides has a significant impact on the physical properties such as high viscosity, stability, and miscibility in polar solvents. Castor oil can be used as a viscosity modifier in polymeric materials. The structure of castor oil such as the trifunctional nature contributes to the toughness of the oil and the long fatting acid chain to its flexibility for modification. The structural features of castor oil are high solubility, small hydrodynamic diameter, and lower melting point (Veronese et al., 2011).

Most research on castor oil focuses on the hydroxyl group as discussed by Mutlu and Meier (Mutlu & Meier, 2010) who have defined very well the composition of castor oil in terms of ricinoleic acid. The presence of the ricinoleic acid makes the processing much easier because the target is the largest component, whereas, with the other oils, they have two or more major

components, for example, the soybean has oleic (23.26 %) and linoleic (55.53 %) acids, which makes it difficult to separate (Table 4). The other advantage of using castor oil is the fact that it is nonedible and therefore does not compete with food security.

Table 4: Fatty acid composition of some typical vegetable oils against those of castor oil (Chakrabarti & Ahmad, 2008; Ramos et al., 2009; Khan, 2002).

Vegetable oil	**Fatty acid composition (% w/w)**						
	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Ricinoleic C18:1 variety	Linoleic C18:2	Linolenic C18:3	Arachidic C20:0
Corn	6.50 - 11.67	1.40 - 1.85	25.16 - 25.2	0.00	60.60 – 65.6	0.10 - 0.48	0.10 - 0.24
Canola	3.49	0.85	64.40	0.00	22.30	8.23	0.00
Soybean	11.30 - 11.75	3.15 – 3.60	23.26 – 24.9	0.00	53.00 - 55.53	6.10 - 6.31	0.00 – 0.03
Sunflower	6.08 – 6.20	3.26 – 3.70	16.93 – 25.2	0.00	63.10 - 73.73	0.00 – 0.02	0.00 – 0.03
Castor	0.70	0.90	2.80	90.20	4.40	0.20	0.00

2.3.2. Production route of castor oil products

The unique properties of castor oil can be influenced from different chemical reactions by exploiting the different functional groups such as the ester linkage, hydroxyl group, and the vinyl group. These functional groups can be modified through processes such as transesterification, epoxidation, dehydration, pyrolysis, hydrogenation, ozonolysis, sulfation, hydrolysis, and polycondensation (Desroches et al., 2003). The chemical modifications of castor oil are clearly illustrated below in Figure 3. From the versatile list of processes to follow,

the process should be cost effective, energy efficient, green, and less labour intensive. This is because the aspects of health, safety, and environment need to be taken into consideration.

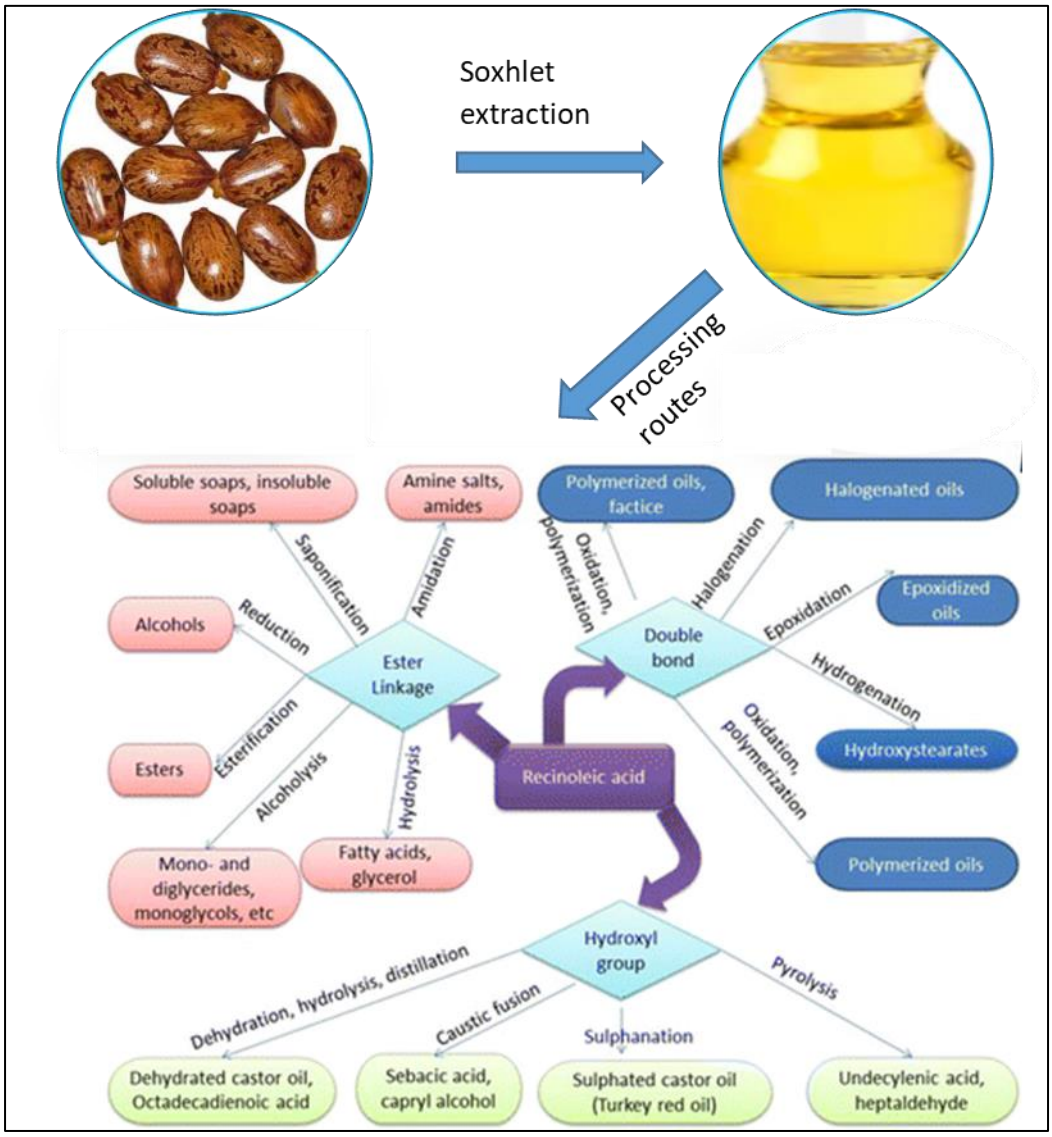

Figure 3: Routes for the synthesis of various products from vegetable oils (Shah et al., 2015; Sharmin & Zafar, 2009; Wool, 2005; Mubofu, 2016)

Hydrogenation

The process of hydrogenation involves the introduction of a hydrogen atom to the unsaturated fatty acid in the presence of a catalyst (e.g. nickel or palladium; Figure 4). The hydrogen converts the ricinoleic acid into a saturated 12-hydroxystearic acid that is semi-solid. The semi-solid material (wax-like) is highly used in the industry for polymer materials (Mubofu, 2016).

Catalytic transfer hydrogenation (CHT) is another route for the hydrogenation of castor oil. The advantage with CHT is that it can be used at ambient temperatures and pressures in organic solvents, therefore leading to less energy consumption. The CHT does not require distinct reactors and the solvent used can also be used as a hydrogen donor in the presence of a catalyst.

The temperatures that are often used for hydrogenation range from 115°C to 180°C; temperatures are low due to the presence of the catalyst, and therefore less energy is required in the process (Alwaseem et al., 2014). Hydrogenated castor oil is insoluble in water and organic solvents at ambient temperature; however, it is soluble at high temperatures and therefore highly recommended for industries. Hydrogenated castor oil has enhanced thermal and oxidative stability (Mubofu, 2016). Hydrogenated castor oil also has a longer shelf life and it is odourless and tasteless. The hydrogenated castor oil and its derivatives are used for plasticizers of nitrile rubbers because of optimum tensile strength, elongation at break, and the resistance of rubber to swelling due to other oils (e.g. motor oil) that it can interact with. In lubricant, paint, cosmetic, and miscellaneous industries, hydrogenated castor oil is used (Yousef et al., 2001).

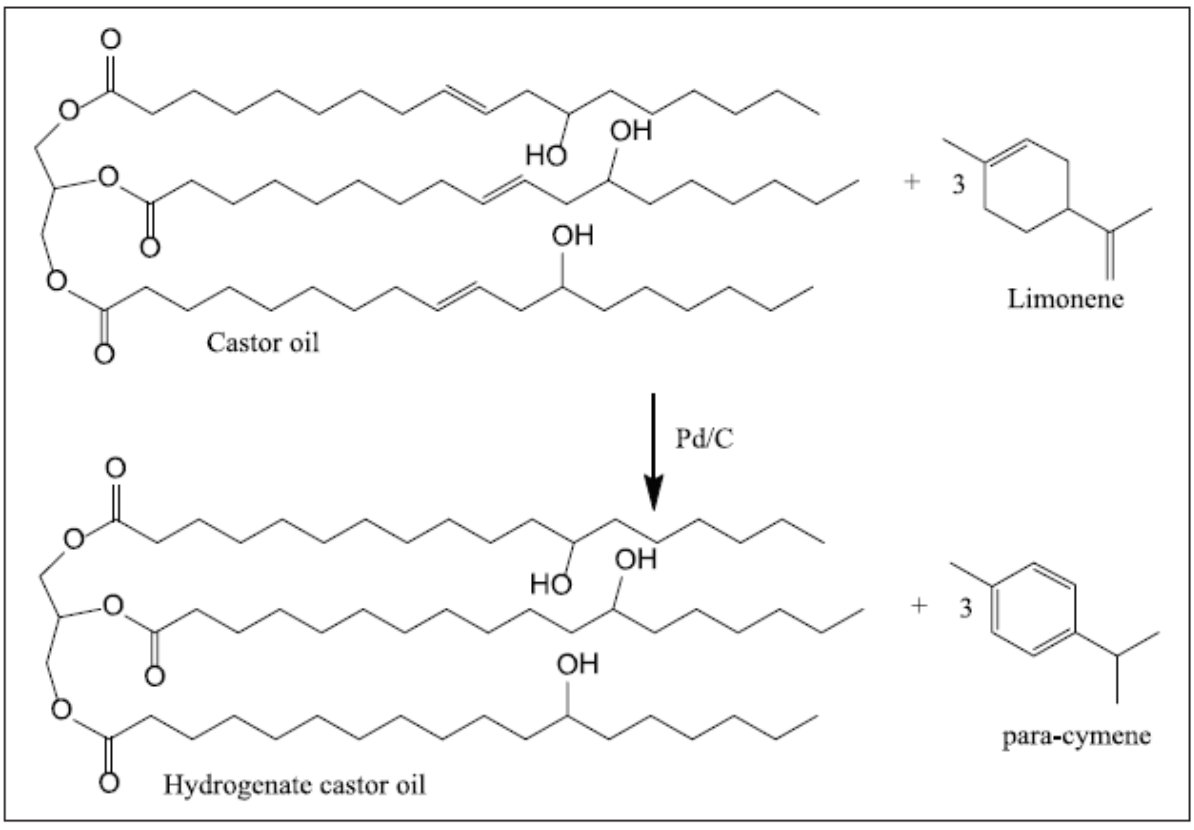

Figure 4: Schematic representation of the Hydrogenation of castor oil (Mubofu, 2016)

Pyrolysis

Pyrolysis is a highly recommended thermal method that is used for the conversion of biomass in the absence of oxygen into solid (char), liquid, or gaseous phases (Li et al., 2017). The pyrolysis of castor oil splits the molecule to produce undecylenic acid and heptaldehyde. In the presence of air, the biomass will undergo combustion and give off carbon dioxide (CO_2) as a product. The process is conducted at high temperatures ranging from 345°C to 752°C, and the pyrolysis bio-oil is obtained (Chen et al., 2014) (Figure 5). The review of pyrolysis of various oils has been reported (Chen et al., 2014).The presence or absence of a catalyst determines if the product will have a higher or lower molecular weight (i.e. more like diesel or gasoline). The pyrolysis of vegetable oils in the presence of a catalyst is much more common than direct thermal cracking and the main catalysts can be grouped into the following types: (a) molecular sieve catalysts, (b) activated alumina catalysts, (c) transition metal catalysts, and (d) sodium carbonate (Chen et al., 2014).

Pyrolysis of castor oil usually takes place at 350°C for approximately 30 min in the pressure range of 1.47–1.96 MPa (Chen, et al., 2014). The castor oil can be converted into petrochemical feedstock (biodiesel) using thermal energy through a process called thermal cracking (Chen et al., 2014; Sánchez et al., 2015). However, an increase in temperature results in a decrease in density as indicated in Table 5 (Deshpande et al., 2013). This process is energy intensive due to extremely high temperatures, and therefore this might affect the cost of production. This is also a multi-step process that will require a large processing plant.

Fast pyrolysis produces up to 80 wt. % liquid on dry feed. The remaining 20 wt.% is from gaseous products consisting of aerosols, true vapours, non-condensable gases, and solid char (Bridgwater & Peacocke, 2000). The bio-oil from pyrolysis is dark brown in colour (Bridgwater, 2003) . Some of the major disadvantages of using the bio-oil as the diesel fuel are its low higher heating value (HHV) which is approximately 40% less than that of the fuel oil, high viscosity, and substantial amount of solid content (Bridgwater, 2003).

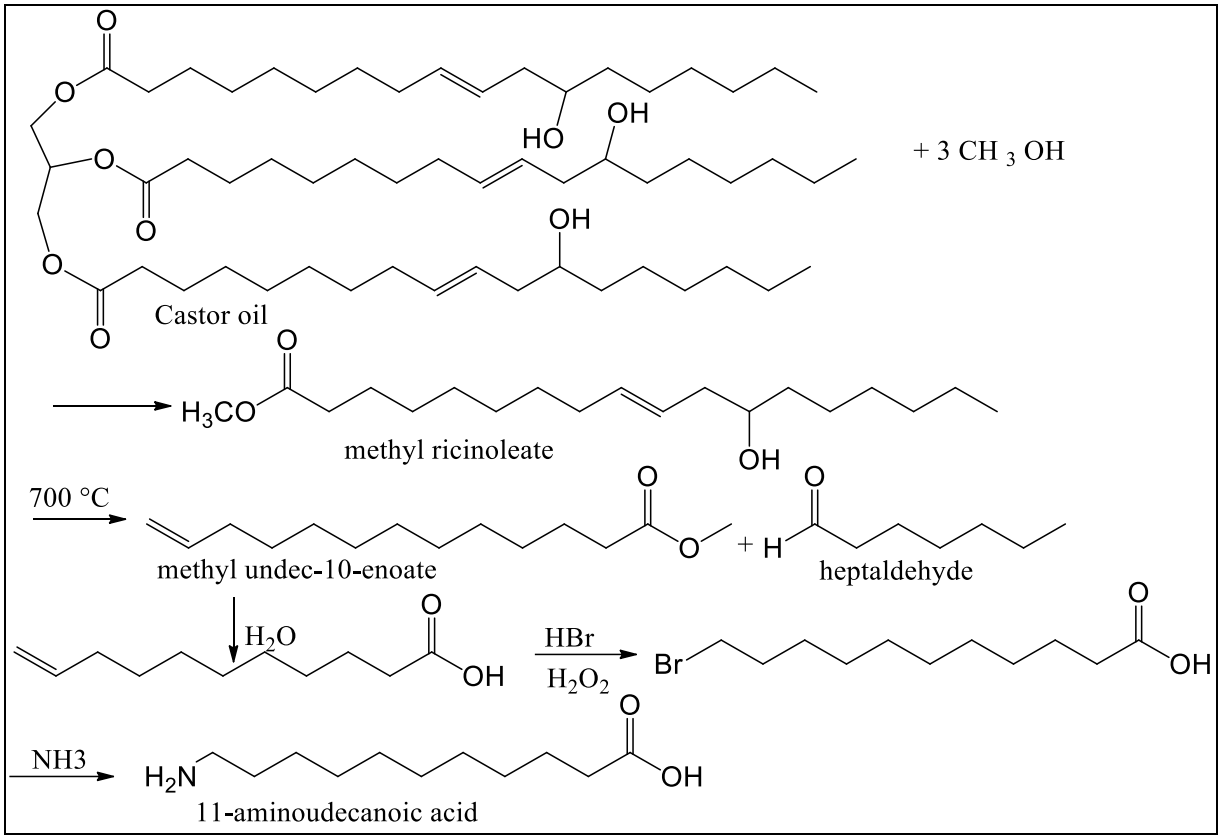

Figure 5: Schematic representation of the Pyrolysis of castor oil (Mubofu, 2016)

Table 5: Effect of temperature on density when using pyrolysis.

Sample	**Temperature (°C)**	**Density (g/ml)**
1	350	0.84
2	400	0.832
3	450	0.82

Hydrolysis

The hydrolysis of castor oil is usually conducted through the addition of sodium hydroxide (80wt%) at approximately 250 - 360 °C results in the formation of glycerol and ricinoleic acid that can be further converted into sebacic acid and capryl alcohol. Sebacic acid is used as a monomer for the synthesis of nylon when reacted with hexamethylene-diamine as shown in

Figure 6. The alcohol is often used as a solvent, dehydrator, floatation agent and anti-bubbling agent (Bridgwater, 2003). The positive outcome of this process is that it is a green process because water is used in the process, hence it is a more environmentally friendly alternative.

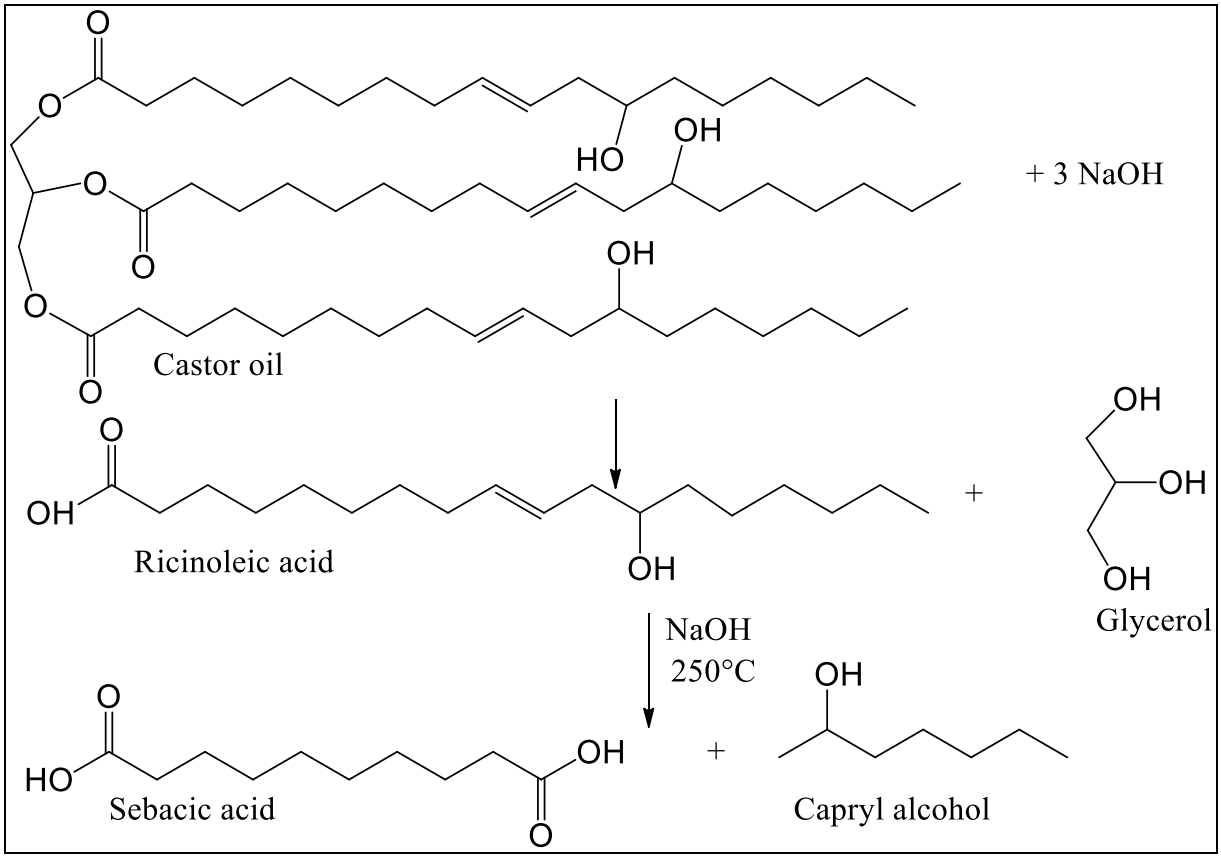

Figure 6: Schematic representation of the Hydrolysis of castor oil (Puthli et al., 2006)

Dehydration

In this process, ricinoleic acid, which is a major component of the castor oil, is reacted with an acid, such as sulfuric acid or phosphoric acid, which acts as a catalyst, to remove the hydroxyl group and introduce a vinyl group as seen in Figure 7. This process is performed at approximately 250 °C under vacuum (Goswami, et al., 2012). The removal of the hydroxyl group requires less energy due to the boiling point of water (100 °C), and, at any temperature above the boiling point, already there should be a certain level of water removed.

Castor oil has only one double bond in each fatty acid chain and so it is classified as non-drying oil. However, it can be dehydrated to give semi-drying or drying oil which is used extensively

in paints and varnishes. Being a polyhydroxy compound, its hydroxyl functionality can be reduced through dehydration or increased by inter-esterification with a polyhydric alcohol (Mubofu, 2016).

Dehydrated castor oil is of significance because coatings that incorporate castor oil alone will never achieve complete cure through oxidative cross-linking as do coatings that contain oil with conjugated double bonds in their fatty acid components. The dehydrated castor oil is often used as a lubricant (Klein, et al., 1995).

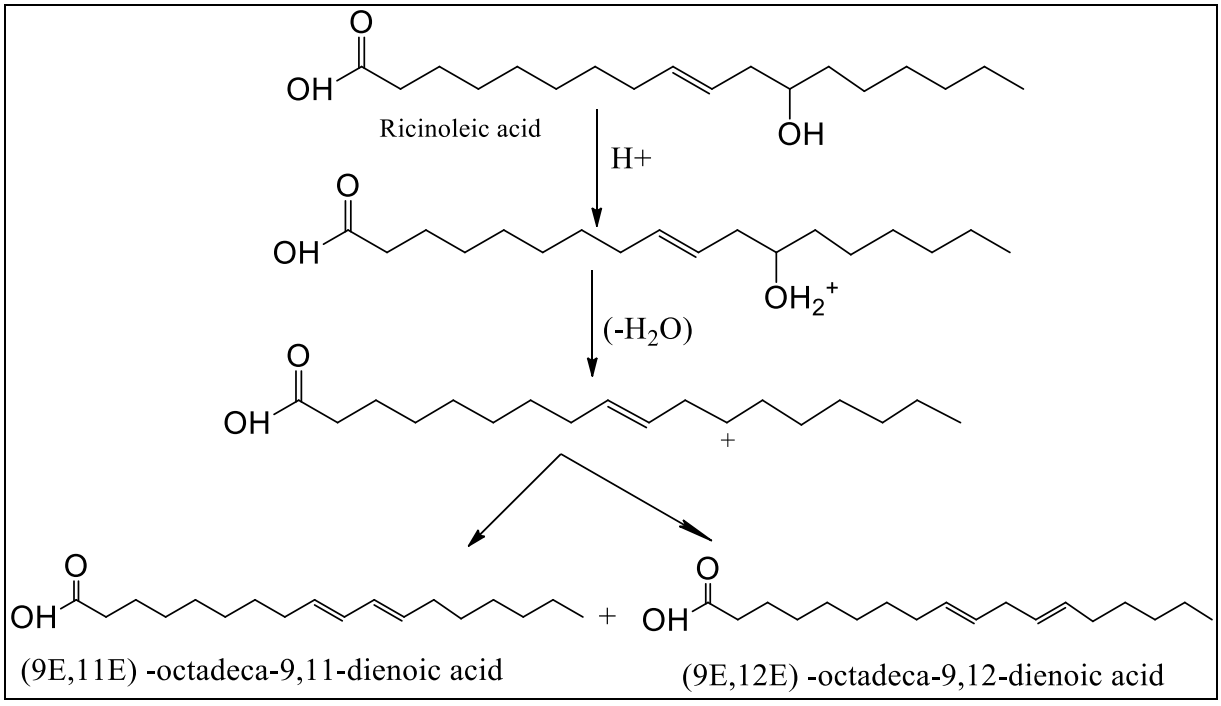

Figure 7: Schematic representation of the Dehydration of castor oil (Bhowmick & Sarma, 1977)

Ozonolysis

Ozonolysis is one of the methods used for the synthesis of polyols from bio-oils that are derived from plants (Figure 8). In this process, ozone is used as a strong oxidizing agent to cleave and

oxidize alkenes that are then reduced to alcohols by a strong reducing agent such as sodium borohydride ($NaBH_4$) (Dotan, 2014). Ozonolysis is the only oxidative cleavage method that is currently used in industries because it is a clean reaction carried out at low temperatures (25°C – 45 °C) without catalyst and the decomposition occurs at 60 °C – 100 °C (Scrimgeour, 2005).

Ozonolysis of vegetable oils yields aldehyde functionalities that by posterior reduction yields a polyol with almost three hydroxyl groups per molecule, however not for saturated fatty acids in the oil. This ozonolysis procedure has been successfully applied to soybean oil, castor oil, canola oil, and triolein; these oils resulted in polyurethanes with improved mechanical properties and higher glass transition temperature compared to the polyurethanes produced from epoxidation (Nieto, 2011). The downside of this process is the fact that ozone is highly reactive; therefore, this can result in many side reactions that can form multiple byproducts if the process does not take place in strictly controlled environments. However, the use of a catalyst means that less energy will be required (Figure 8).

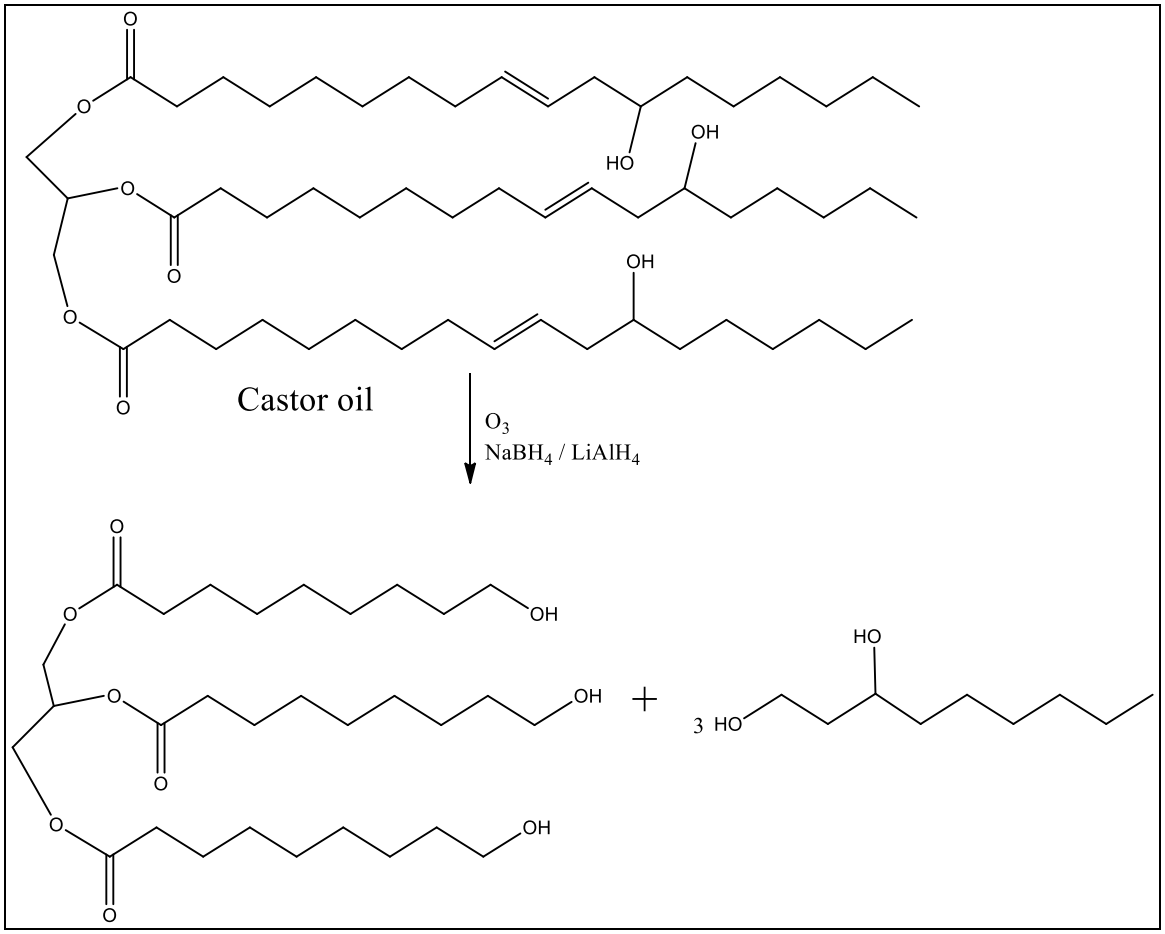

Figure 8: Schematic representation of the Ozonolysis of castor oil (Cvetkovic et al., 2008)

Epoxidation

Epoxidation reactions are usually conducted using a peracid (peroxy acid), either preformed or formed in situ, by reacting a carboxylic acid (usually acetic acid) as an oxygen carrier with hydrogen peroxide (H_2O_2) as an oxygen donor. Formic acid is preferred compared to acetic acid as the oxygen carrier due to its high reactivity and no need to use a catalyst in the formation of performic acid (Vaidya et al., 2012; Derawi & Salimon, 2010). Different kinds of catalysts such as enzymes, Ti(IV)-grafted silica catalysts, acid catalysts, tungsten-based catalyst, transition metal complexes, and ion exchange resin are used for epoxidation (Mahla, 2014)

The products obtained from epoxidation are known as oxirane compounds or epoxides. Epoxidation of vegetable oils is a commercially important reaction because the epoxides obtained from vegetable oils and from their alkyl esters have their applications in such materials as plasticizers and polymer stabilizers. Moreover, the epoxides can be used as intermediates in the production of a variety of derivatives because of high reactivity of the strained epoxide ring (Patil & Waghmare, 2013). Epoxidized castor oil is also applied in high-temperature lubricants, polyurethane dispersions, paints, coatings and adhesives, nanocomposites, surfactants, hydraulic oils, and biodiesel (DeHonor Márquez et al., 2018). Figure 9 illustrates the epoxidation reaction. The process is versatile because it can use multiple catalysts that are both biological and inorganic. The presence of the catalyst makes the process less energy intensive.

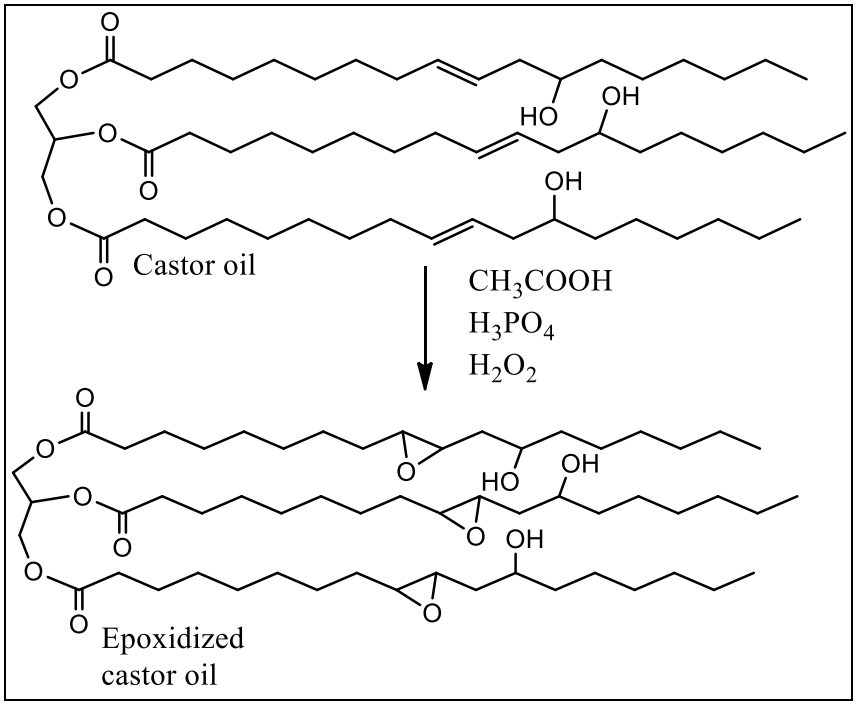

Figure 9: Schematic representation of the Epoxidation of castor oil (De Luca et al., 2009)

Transesterification

The process involves reacting an alcohol with an ester that is present in the castor oil. This process is performed in the presence of a catalyst that can be either an acid or a base though often acid catalysts are used (e.g. hydrochloric acid, sulfuric acid, etc.). This process is reversible and, to avoid this, excess alcohol is used to shift the reaction to completion. The products formed in this process are glycerol and biodiesel (methyl ricinoleate) (Mubofu, 2016; Deshpande, et al., 2013; Patil & Waghmare, 2013).

The transesterification of castor oil can be achieved in the presence of a catalyst (e.g. KOH; Figure 10) (Mahla, 2014). Deshpande et al. (Deshpande et al., 2013); varied the methanol ratio, reaction time, and concentration of the catalyst in their process; the concentration of the catalyst resulted in increased kinematic viscosity and specific gravity, however with decreasing acid value and Saponification value; which represents the amount of potassium in milligrams that is required to saponify a gram of fat under specified conditions; whereas Chakrabarti and Ahmad (Chakrabarti & Ahmad, 2008) also varied the same parameters as Deshpande et al. (Deshpande et al., 2013) and obtained the same outcome.

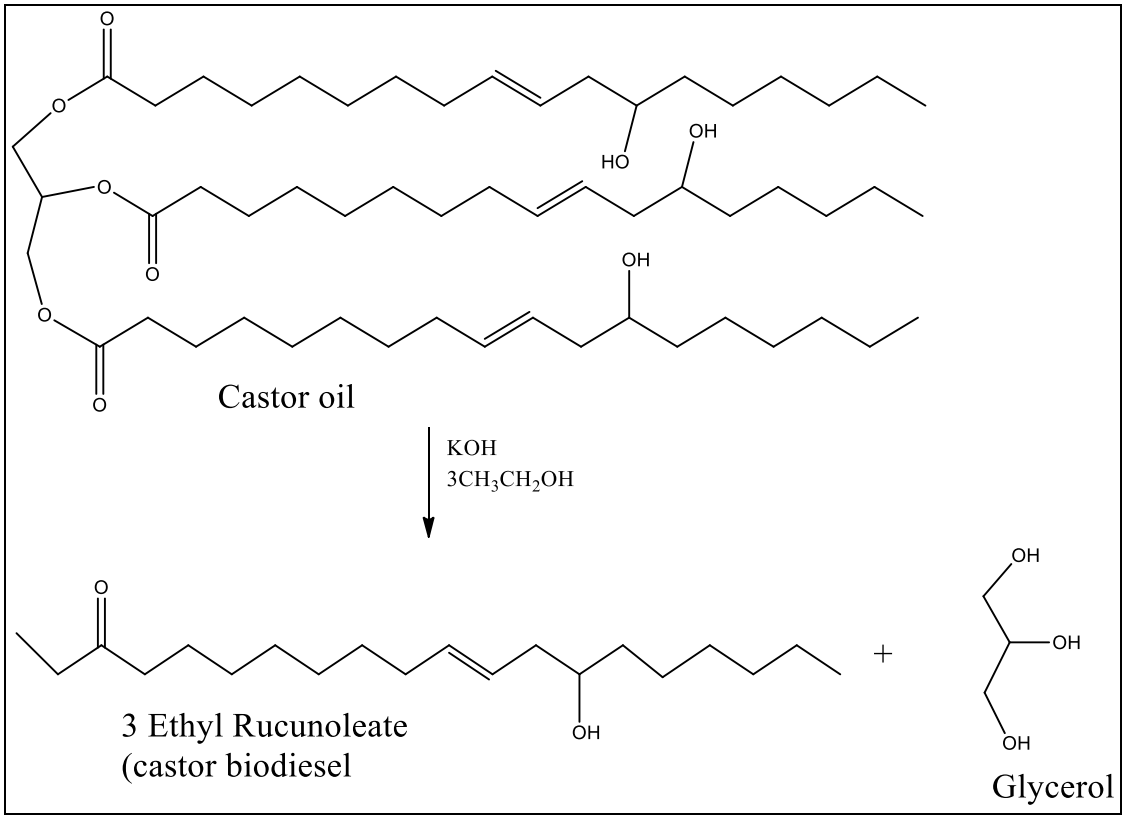

Figure 10: Schematic representation of the Transesterification of castor oil (Cavalcante et al., 2010)

Sulfation

Sulfated castor oil, also known as Turkey Red Oil due to the sulfur reddish color, is one of the first chemical derivatives of castor oil. Sulfated castor oil is developed through the addition of concentrated sulfuric acid at the same rate to castor oil for a few hours with constant cooling and agitation at 25°C–30°C. After completion of the reaction, the product is neutralized using a base solution or an amine. This process uses room temperature and this is because of the application of a very strong acid that does not require high temperatures to react. The acid might need to be diluted in most instances to ensure that the process is not extremely hazardous (Figure 11).

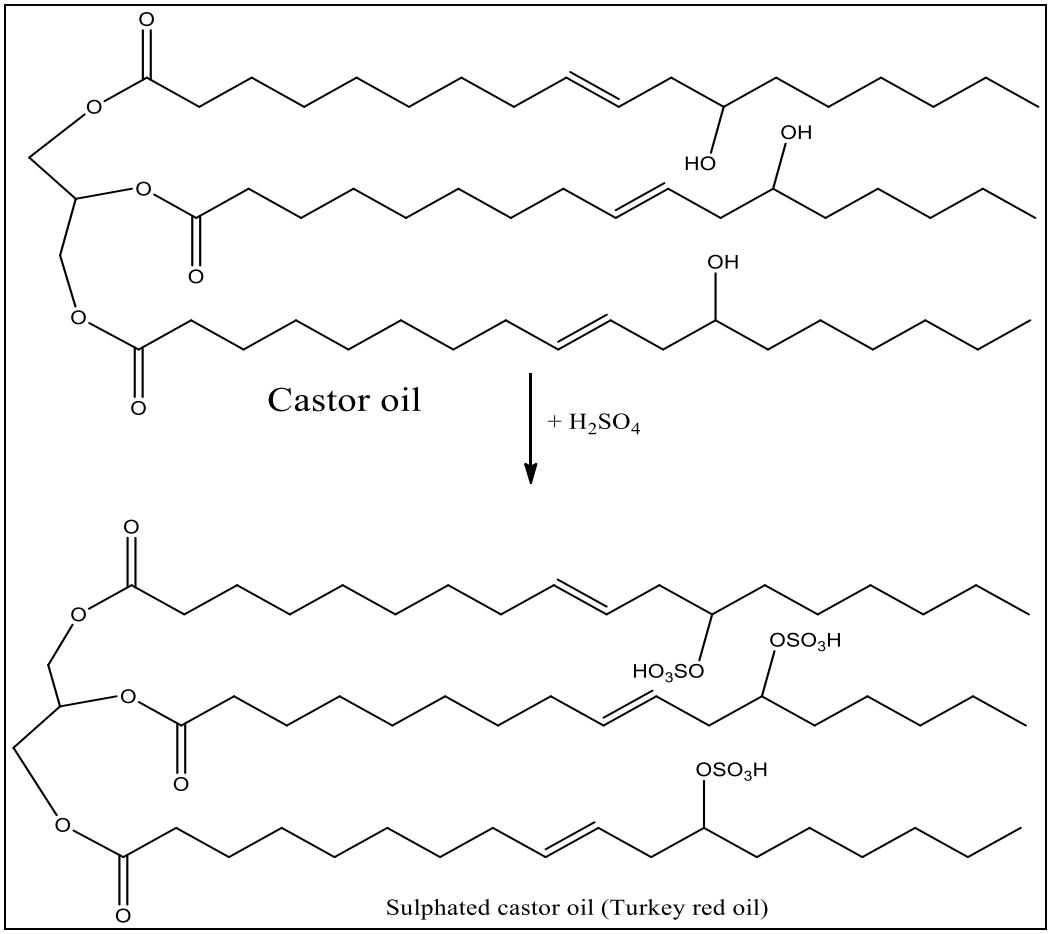

Figure 11: Schematic representation of the Sulfation of castor oil (Prasad & Rao, 2017)

Polycondensation

Polycondensation, also known as condensation polymerization is defined as the process of synthesizing polymers through condensation reaction of organic materials. During condensation, the smaller molecules are fragmented. In polycondensation, the small fragments known as monomers chemically react to form longer chains with higher molecular weight. The monomers need to have two functional groups which is the average required number of reacting groups in each molecule. The generation of lower molecular component affects the kinetics of polycondensation because the concentration and the mass of the molecule will affect the reaction mechanism negatively. The best way to counter the effects of negative reaction mechanism is to perform reactions at higher temperatures and deep vacuum, this will also reduce by-products (Bhat & Kandagor, 2014)

2.4. Bio-binders

The composition of plant oils such as castor oil allows for the development of bio-binders. Bio-binders also known as biopolymers are the compounds acquired from natural resources such as plants and contain monomers that are linked by covalent bonds to form polymeric chains. The castor oil–based biopolymers are usually in the form of polyurethanes, polyamides, polyethers, and polyesters (Mubofu, 2016).

Bio-binders are used as the glue in simple terms for different materials. Bio-binders are different based on their melt flow indices, impact properties, hardness, vapor transmission characteristics, coefficient of friction, and decomposition. There are other engineering properties that are also of significance in bio-binders such as tensile strength, tensile modulus, flexural strength, flexural modulus, and density (Asokan et al., 2012). The ability of bio-binders to absorb water is also an important parameter, especially during the synthesis of the binder because water is a green solvent and is cheaper.

2.4.1. Properties of bio-binders

The materials that are made from different composites are used for various applications and density is considered one of the most important properties as it determines where the binder will be applicable. Bio-binders are often classified according to their mechanical properties as illustrated in Table 6. The densities of the bio-binders that are available in the market normally range from 0.25 to 1.26 g/cm^3 (Oksman et al., 2003). The bio-binders that have low densities are mostly preferred in various industries because of various reasons such as energy efficiency, ease of handling, and relatively low costs (Asokan et al., 2012).

The tensile strength of bio-binders is also one of the properties considered in the industry. The tensile strength of different biopolymers ranges between 5.9 and 72 MPa (Chanprateep & Kulpreecha, 2006). Tensile modulus is another important mechanical property of bio-binders because it is the measure of the stiffness of the polymer; P-4-Hb has a tensile modulus of 0MPa

meaning that the polymer cannot resist elastic deformation. The market-related tensile modulus of the bio-binders ranges between 0.4 and 7.7 GPa (Asokan et al., 2012).

Elongation is another property of bio-binders that determines the amount of deformation that happens to the polymer when subjected to stress. The lowest elongation percentage reported is 1.0% and the highest was found to be 3.0% (Asokan et al., 2012). Research has shown that there is considerable variation in densities and elongation of different bio-binders and therefore there is a need to develop different synthetic methods for the development of new binders that will be considered for new technologies as research advances.

Table 6: Types of bio-binders and their mechanical properties (Mahla, 2014)

Types of Bio-Binders	Density (g/cm^3)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation (%)
1. Polylactic acid (PLA)	1.26	5.9 – 7.2	1.08 – 3.61	2.1 – 30.7
2. Polyhydroxybutyrate (PHB)	1.2 – 1.5	24 – 40	3.5 – 7.7	1.56 – 6
3. Poly-3-hydroxybutyrate (P-3-Hb)	1.28	40	3.5	0.4 – 6
4. Poly-3-hydroxybutyrate-co-3-hydroxyvalerate (P-3-Hb-Hv)	0.22 – 0.25	23 – 40	3.5	1.6 – 20
5. Poly-4-hydroxybutyrate (P-4-Hb)	1.22	104	0	1000
6. Polycaprolactone (PCL)	1.13	16 - 23	0.4	> 700

The inability of a binder to absorb water show that there has been increased cross-linking densities and therefore the more cross-linking takes place, the stronger the binder as illustrated in Figure 12. This therefore means that less water will be retained in the binder and making the binder less susceptible to volatility and spontaneous reactions with other materials (Shaik et al., 2015; Petrović et al., 2004)

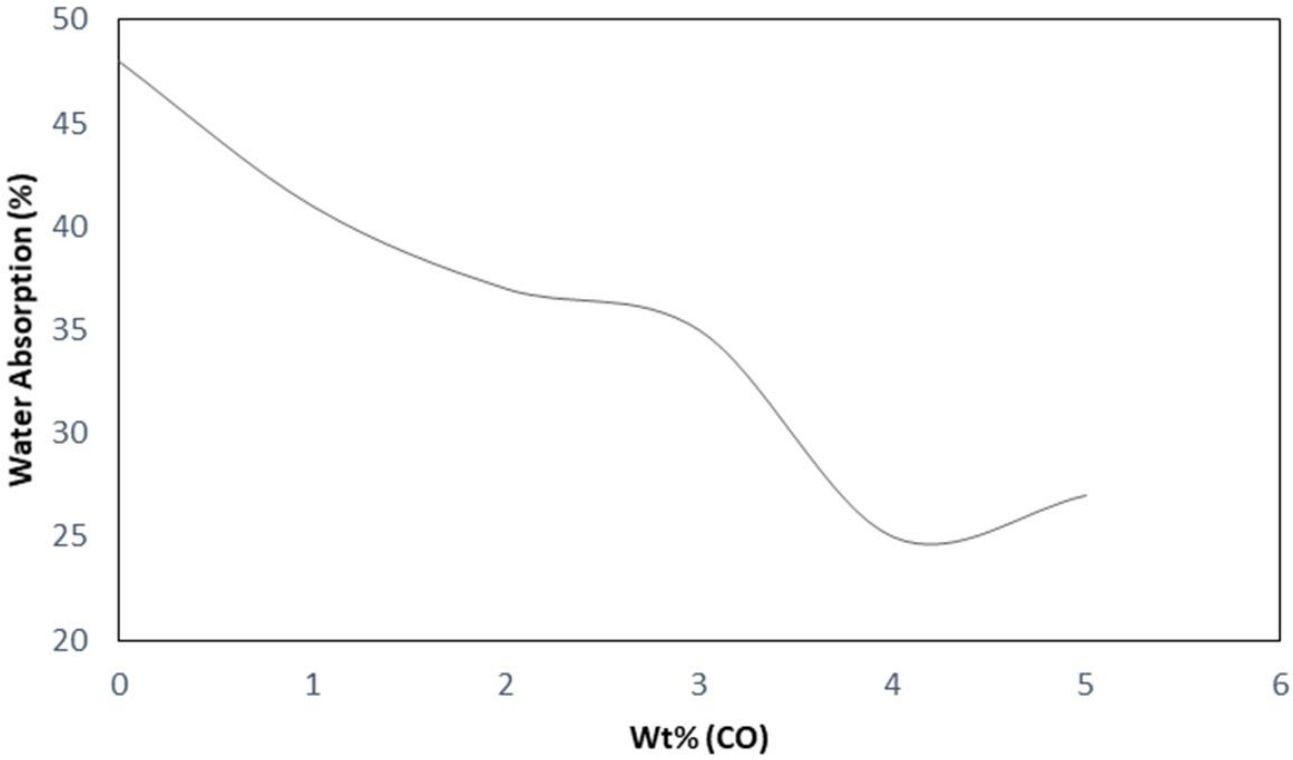

Figure 12: Effects of dosage of CO on water absorption rate of the binder (Petrović et al., 2004)

The binder that contains castor oil behaves better than the one without the castor oil and therefore resulting in better stability as seen in Figure 13 whereby the elongation break is reduced with increased castor oil (Luo et al., 2011).

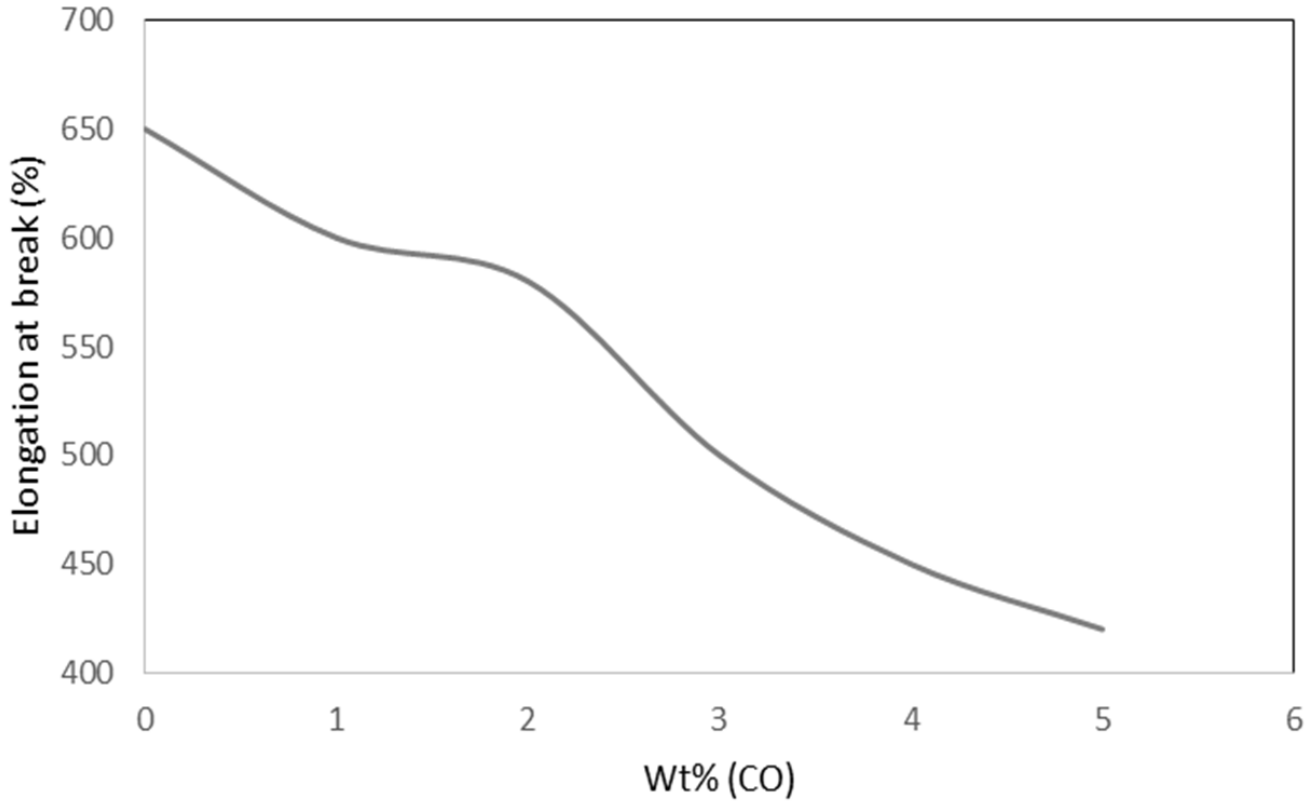

Figure 13: Effects of dosage of CO on elongation of the binder (Luo et al., 2011)

Figure 14 illustrates that the binder will have higher tensile strength as the castor oil loading is increased, this therefore means that the polymer will have higher resistance to break under tension.

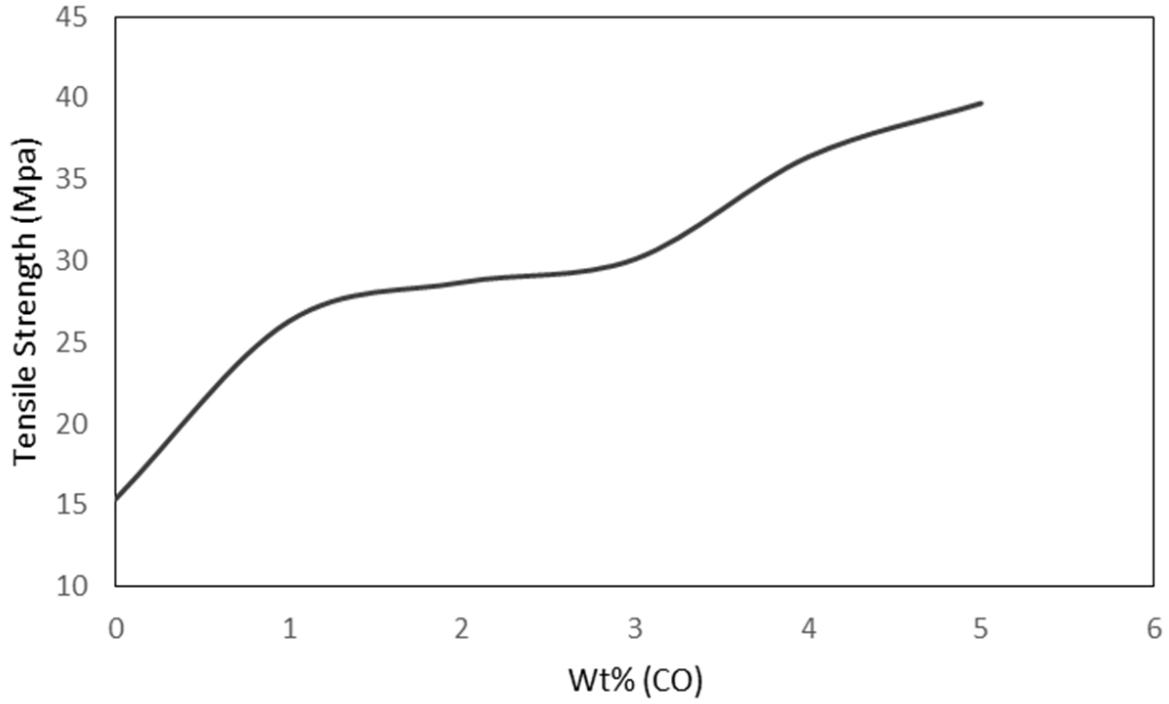

Figure 14: Effects of dosage of CO on tensile strength of the binder (Luo et al., 2011)

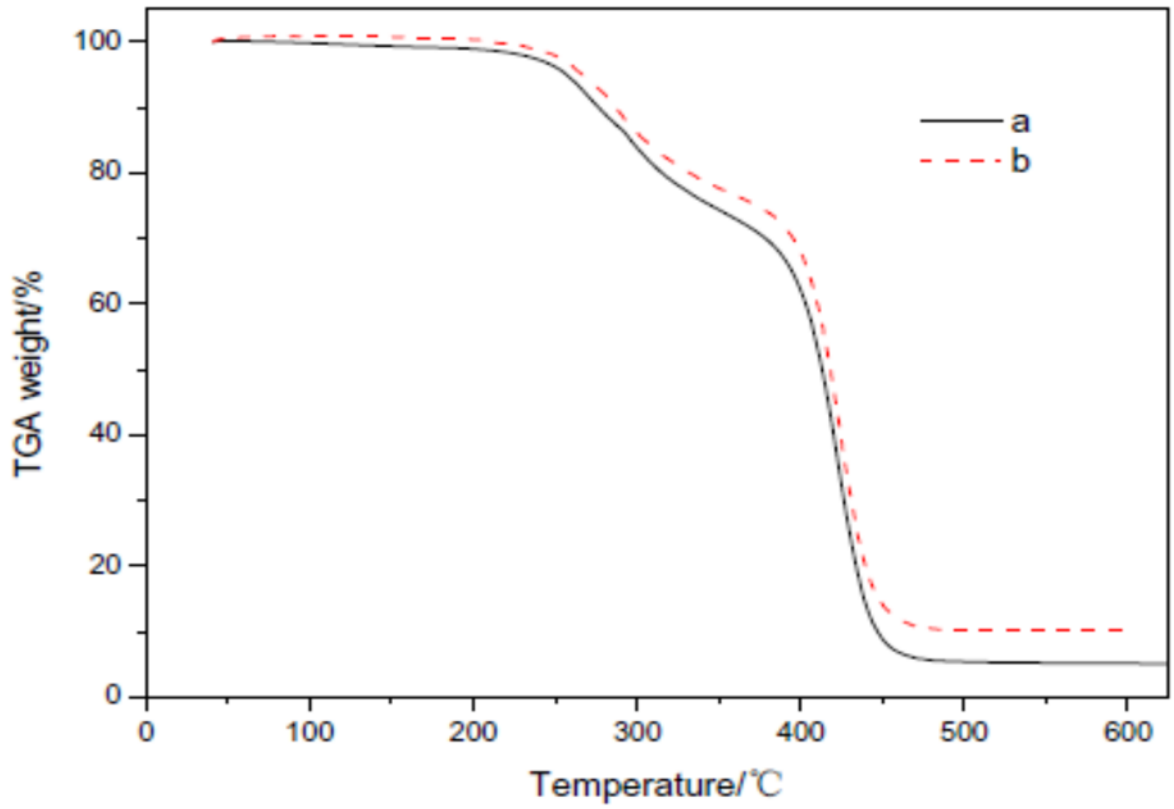

Figure 15: Effects of dosage of CO on stability of the binder where a) No CO and b) 5 wt. % of CO (Luo et al., 2011)

Figure 15 represents the properties of the castor oil whereby if there is Increased cross-linking between the castor oil and polyurethane, the polymer takes longer to decompose (Luo et al., 2011)

2.4.2. Application of bio-binders

Bio-binders are used in multiple industries for different applications such as drug delivery system, wound healing, food containers and agricultural films, waste bags, soil retention sheeting, filtration, hygiene and protective clothing (Asokan et al., 2012), paper industry, wood-to-wood bonding (Ibrahim et al., 2015), and automotive industries (Akampumuza et al., 2017). Castor oil–based bio-binders have been reported to have been applied in launch vehicles and missile propellants60 and also in the development of asphalt bio-binders for pavements in civil engineering (Xiu & Shahbazi, 2012; Venema, 2012). The properties are outlined below, which allow for the application of bio-binders in different industries. Figure 16 clearly illustrates most industries that are using bio binders.

Figure 16: Application of binders in various industries (OrganoClick, 2019)

Chapter 3. Methods and Analytical techniques

In this research, the development of the process of preparation and characterization of castor oil based bio-binders was studied as outlined below. Three synthetic methods (Polycondensation, Ozonolysis, and Epoxidation) were utilized in this study. Different parameters such as variations in temperature, concentration of castor oil and different catalysts will be studied for the optimization of each synthetic route. At the end of this study, the three synthetic methods will be discussed and based on this study, a suitable synthetic route for the preparation of castor oil based bio-binders will be proposed.

3.1. Polycondensation process

Polycondensation; also known as step-growth polymerization; is a chemical reaction whereby a larger molecule with increased molecular mass is formed and smaller molecules such as water are removed. Polycondensation can be broken into two words; 'poly' meaning that a chain of reactions occurs, and 'condensation' meaning that there is a condensate (water or alcohol) formed (Ramakrishnan, 2014).

3.1.1. Materials

Castor oil from SSD in South Africa, Sodium methoxide from Sigma Aldrich (reagent grade, 95% pure) and/or Sodium hydroxide from Sigma Aldrich (reagent ≥ 97%), Methanol from Sigma Aldrich (anhydrous, 99.8%), Diethanolamine from sigma Aldrich (reangent grade, ≥ 98%, Terephthalic acid from Sigma Aldrich (98% pure), Butane from Sigma Aldrich (≥99% pure), isopropanol from Sigma Aldrich (≥99.5% pure), and toluene-2-4-diisocyanate (TDI) from Sigma Aldrich (95% pure), Methylene diphenyl diisocyanate (MDI) from Sigma Aldrich (97% pure), diisopropyl ether from Sigma Aldrich (98% pure), soudium chlorise (NaCl) from Sigma Aldrich (reagent grade, ≥99% pure), diethyl ether from Sigma Aldrich (reagent grade, ≥99% pure), Xylene from Sigma Aldrich (reagent grade, ≥98.5% pure) and layer chromatography (TLC) plates from LabFriend in South Africa.

3.1.2. Experimental procedure

A three-step experimental procedure was adapted as below (Shaik, et al., 2015):

a. Synthesis of N, N-Bis (2-hydroxyethyl) Castor Oil Fatty Amide (HECA)

- A round bottom flask with a stirrer, dropping funnel and thermometer was used. Diethanolamine (50 g) and sodium methoxide (0.26 g) were added into the flask.
- This was followed by a dropwise addition of Castor oil (60 g) at a temperature range of 120 ± 5 °C.
- Thin layer chromatography (TLC) was used to see how far the reaction has progressed. This was done by placing the product on the stationary phase which is the silica layer on the TLC and apply a mobile phase of diisopropyl ether.
- When the reaction had reached completion, diethyl ether and 15% aqueous NaCl solution were used to wash the resultant mixture, which was then dried with anhydrous sodium sulphate.
- The diethyl ether was left on the bench to evaporate overnight and the product; HECA; was obtained

b. Castor Oil Polyesteramide (CPEA)

- HECA (0.01 mol) and terephthalic acid (0.07 mol) were dissolved in 100mL of xylene. A three-neck round bottom flask that was used containing a dean stark trap, N_2 inlet, thermometer, and stirrer for agitation.

- The temperature used was 250°C and progress of reaction was monitored by TLC and acid value (low pH required)
- Once reaction has reached completion, the product was left on the bench overnight to evaporate the solvent and to obtain CPEA.

c. Castor Oil Polyurethane - esteramide (UCPEA)

- CPEA and TDI (13 wt. %), were mixed together in the presence xylene using a four-neck flask operating under N_2 atmosphere at 120°C with a magnetic stirrer inside.
- TLC was used to monitor the reactionat regular intervals of time.
- The time was varied (1, 2, 3, and 4 hours) to get the optimum conditions

3.1.3. Synthesis flow diagram

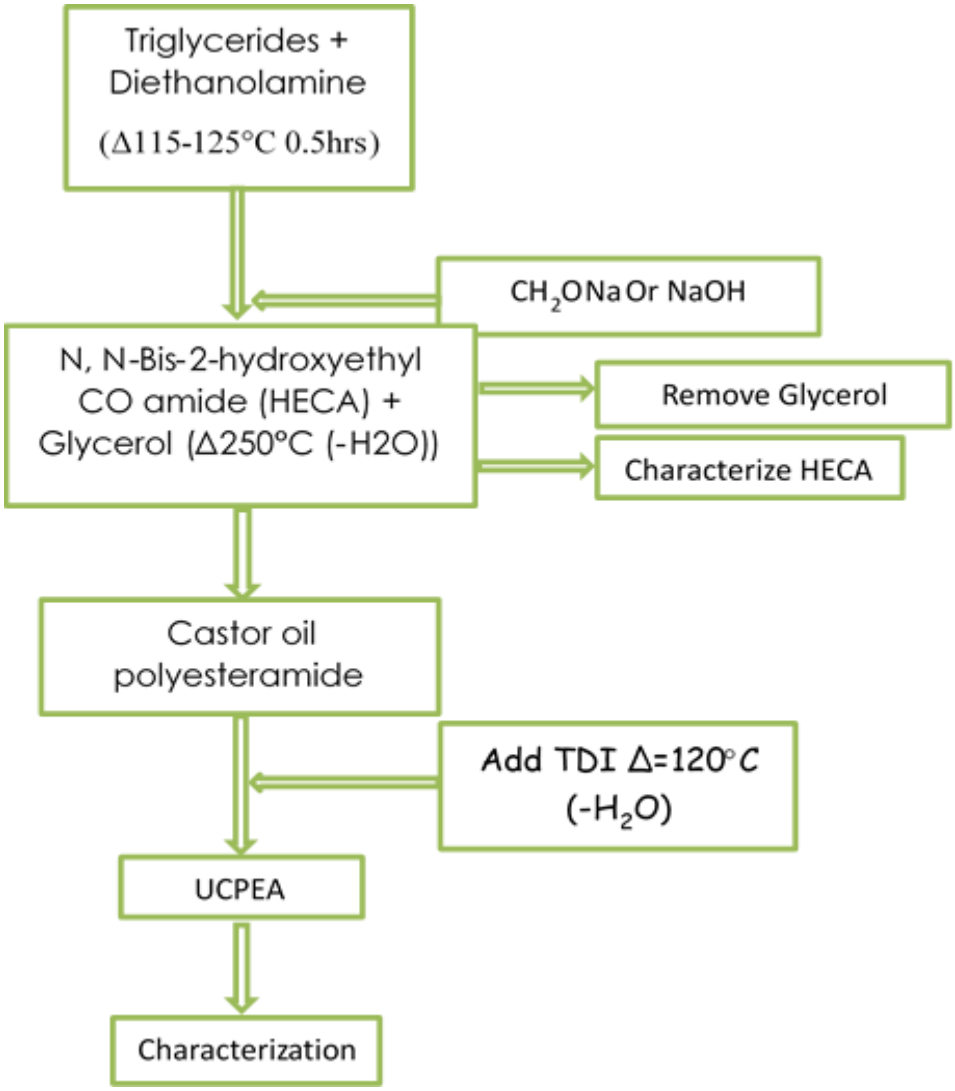

Figure 17: Flow diagram for production of Castor oil based binder from polycondensation

3.2. Ozonolysis Process

Ozonolysis is one of the methods that is used for the synthesis of polyols from bio-oils that are derived from plants. In this process, ozone is used as a strong oxidizing agent to cleave and oxidize alkenes that are then reduced into alcohols by a strong reducing agent such as sodium borohydride ($NaBH_4$) (Dotan, 2014).

3.2.1. Materials

Castor oil from SSD in South Africa, sodium hydroxide (NaOH) from Sigma Aldrich (≥98% pure), Ozone (O_3) with the oxygen cylinder from Afrox and converted to ozone using an ozone generator, sodium borohydride ($NaBH_3$) from Sigma Aldrich (≥98% pure), Methanol from Sigma Aldrich (anhydrous, 99.8%) and methylene chloride from Sigma Aldrich (≥98% pure), phenyl isocyanate from Sigma Aldrich (≥98% pure) and dichloromethane from Sigma Aldrich (anhydrous, ≥98% pure).

3.2.2. Experimental procedure

This was a two-step process as indicated below (Petrović, et al., 2004):

a. Synthesis of Polyols via Ozonolysis

- 10% volume solution in methylene chloride/methanol (55/45 v/v) at -30 to -40°C in methanol-liquid nitrogen was used for the ozonolysis of the castor oil.
- Ozone generator was used to distribute oxygen until the solution turned blue due to the formation of ozone.
- The product obtained from ozonolysis was then reduced by slowly adding sodium borohydride (1/1 molar ratio with equivalent weight) and the temperature was kept at 10-15°C.
- The obtained product (polyol) was purified by washing the reduced mixture with brine until pH was neutral through a pH indicator.
- Anhydrous sodium sulphate was used to try the organic layer
- Solvents and low molecular weight products were left to evaporate overnight at room temperature

b. Preparation of Polyurethanes Based on the Ozonolysis Polyols

- The polyurethanes were mixed in a plastic container using a spatula for 30 seconds to a minute. The preheated polyol at 70°C and freshly distilled MDI at a NCO/OH molar ratio of 1.02 for castor oil-based PU.
- Vacuum was applied to remove bubbles and pour the PU into the mould.
- The samples was dried overnight at 110 °C to ensure that there are no bubble.
- After the initial binder was obtained, the castor oil loading was then varied to obtain optimum conditions (5, 7.5, 10, 12.5, and 20 wt. %)

3.2.3. Synthesis flow diagram

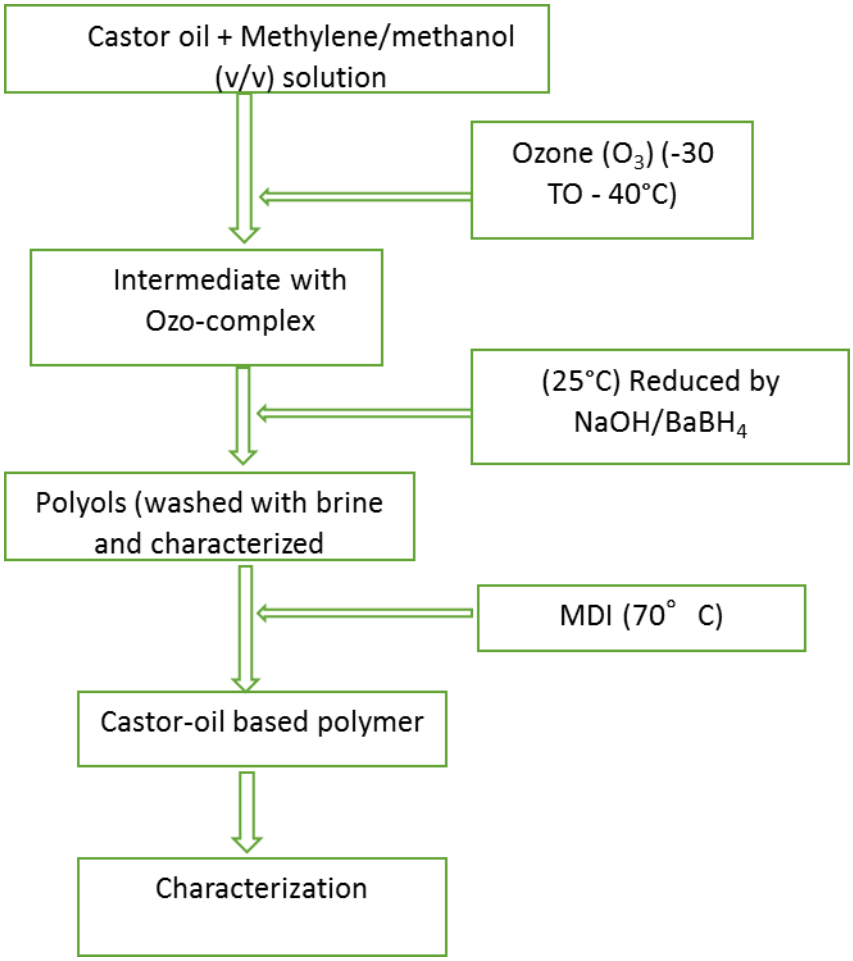

Figure 18: Schematic representation of Ozonolysis and reduction of castor oil

3.3. Epoxidation Process

Epoxidation reactions are usually conducted using a peracid (peroxy acid), either preformed or formed in situ, by reacting a carboxylic acid (usually acetic acid) as oxygen carrier with hydrogen peroxide (H_2O_2) as an oxygen donor. Formic acid is preferred compared to acetic acid as an oxygen carrier due to its high reactivity and no need to use a catalyst in the formation of performic acid (Derawi & Salimon, 2010). As both methods generate peracid, which required more safety attention, in this investigation, alternative method was used.

3.3.1. Materials

Tungstic acid from Sigma Aldrich (99% pure), 30% aqueous hydrogen peroxide (H_2O_2) from Sigma Aldrich, 85% phosphoric acid H_3PO_4 from Sigma Aldrich, cetylpyridinium ammonium chloride from Sigma Aldrich (95%), dichloromethane from Sigma Aldrich (anhydrous, ≥99.8%), Sodium sulphate (Na_2SO_4) from Sigma Aldrich (anhydrous, ≥99%), cyclohexene from Sigma Aldrich (anhydrous, ≥99.5%), polytetramethylene ether glycol (PTMEG, Mn =2000±100) from Merck, 1, 4 -Toluene diisocyanate (TDI-80) from Sigma Aldrich (95% pure) , dimethylol butyric acid (DMBA) from Sigma Aldrich (98%), Nitrogen gas (N_2) from school of chemical engineering, acetone from chemlab supplies (99.9%), and triethylamine (TEA) from Sigma Aldrich (≥99.5%).

3.3.2. Experimental procedure

This was a three-step process whereby firstly the epoxidation catalyst was prepared; secondly, epoxidation of castor oil followed; and lastly the synthesis of the polyurethanes (Luo, et al., 2011).

a. Preparation of the epoxidation catalyst (M)

- Tungstic acid (25 g) was added to 100 ml of 30% aqueous H_2O_2 at 60 °C and the solution was agitated for 60 min.
- This was followed by the addition of 85% H_3PO_4 (2.9 g) dissolved in 10 ml of water at room temperature.
- The solution was diluted with an additional 200 ml of water and agitated for 30 minutes at room temperature.
- To the resultant solution, 18 g of cetyl-pyridinium-ammonium chloride in dichloromethane (400 ml) was added dropwise with stirring over about 20 min.
- Agitation further continued for an additional 60 minutes.
- The organic phase was separated and dried overnight at room temperature
- A dried yellow crystal-like powder was obtained as the product

1. Catalytic epoxidation of castor oil

    - Castor oil (10g), epoxidation catalyst (M) (1g) and H_2O_2 30% (44.4 ml) were all added to a single neck flat bottom flask.
    - The mixture was heated to the desired epoxidation temperature (120 ± 5 °C) through water bath.
    - The mixture was agitated at 1000 ramps per minutes (rpm) for 3 hours.
    - The mixture was filtered to remove the catalyst and obtain the epoxidized castor oil after the removal of the H_2O_2 residue.

2. <u>Synthesis of the polyurethane</u>

- The Epoxidized castor oil (1.0 wt.%) was then mixed with polytetramethylene ether glycol (PTMEG, Mn =2000±100), 1,4-Toluene diisocyanate (TDI-80), and dimethylol butyric acid (DMBA); under an inert atmosphere and controlled temperatures (80 °C) to give the resulting polyurethanes.
- The resultant polyurethanes were the optimised at using different amounts of castor oil (5, 10, 20, 30, and 40 wt.%) for optimum conditions.

3.3.3. Synthesis flow diagram

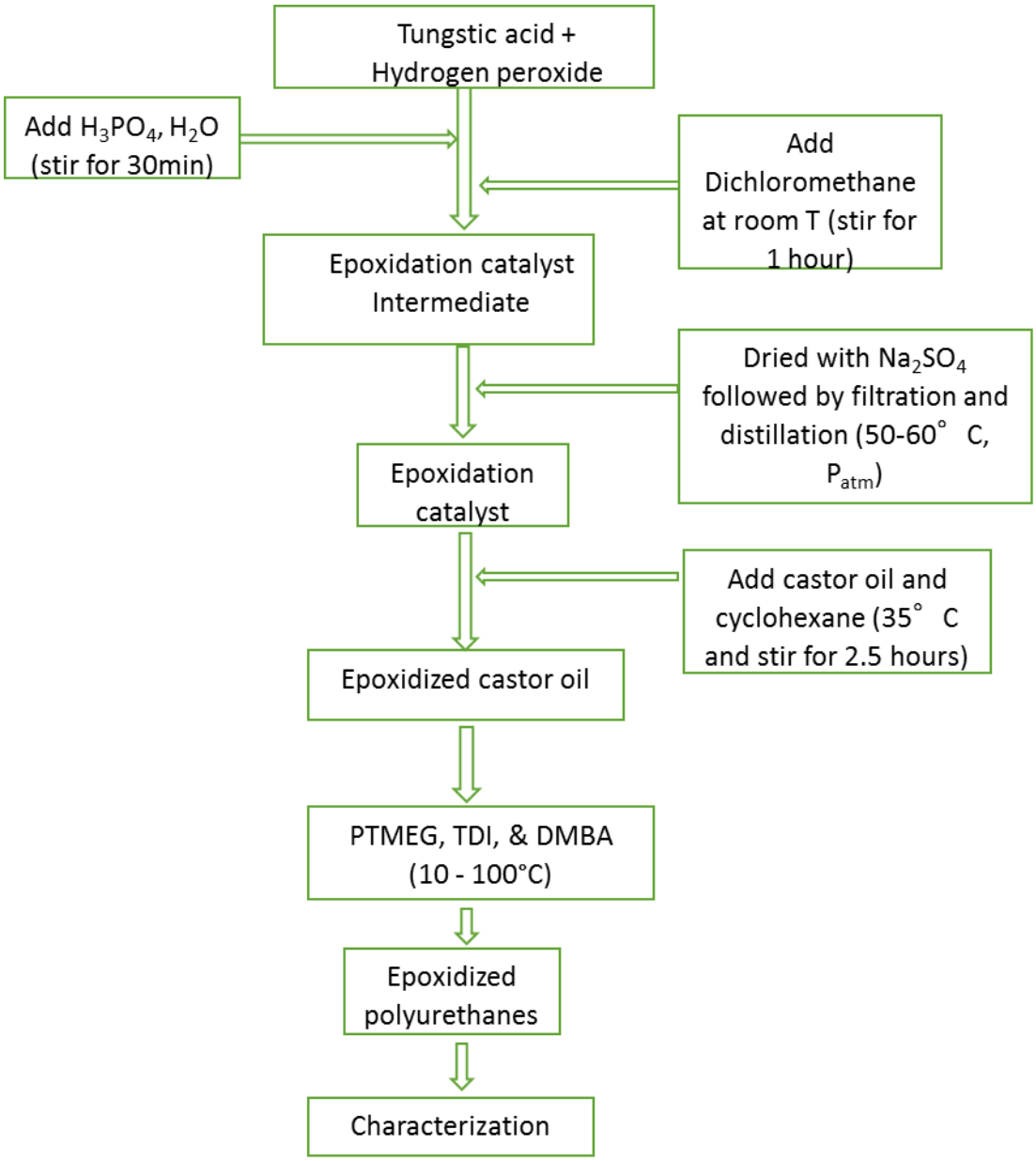

Figure 19: ***Schematic representation of polyurethane synthesis***

3.4. Analytical and characterization techniques

3.4.1. Fourier- transform infrared spectroscopy (FTIR) Analysis

The process required an infrared spectrometer which used a beam to scan through a sample at a certain wavelength to determine the absorbance or transmittance. This was used to enable the determination of different functional groups. The wavenumber was from 450 to 4000 cm^{-1}. The FTIR will be sued to determine if the functional groups that contain binding properties have formed during the synthesis by observing certain peaks at various wavenumbers.

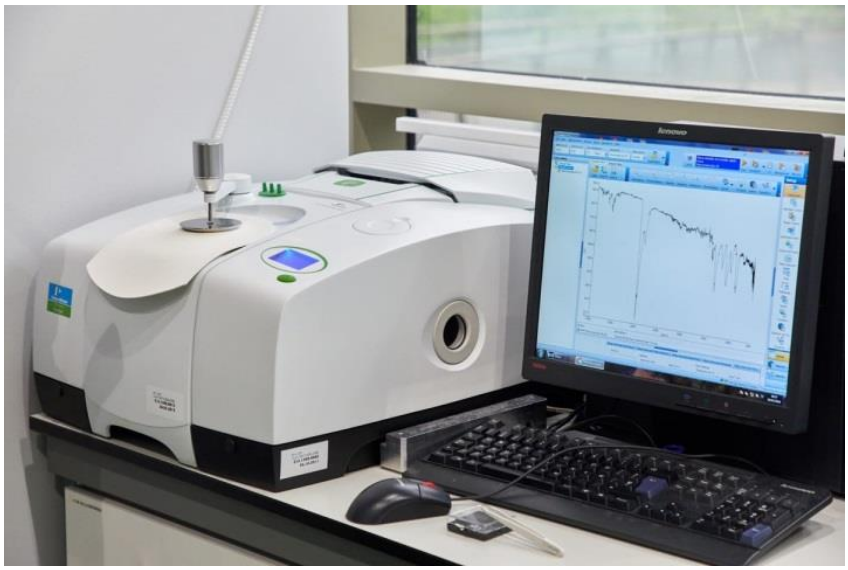

Figure 20: FTIR Frontier instrument from Wits - School of Chemical and Metallurgical Engineering. Supplied by PerkinElmer, United States of America.

3.4.2. Thermogravimetric analysis (TGA)

A Thermogravimeter was used to measure the thermal stability of the material by determining the weight loss of the product under an N_2 atmosphere. The product was heated at different temperature (0 – 600 °C) ranges over a time range.

Figure 21: TGA Q500 instrument from Wits - School of Chemical and Metallurgical Engineering. Supplied by TA instruments, United States of America

3.4.3. Nuclear magnetic resonance (NMR) Spectroscopy

NMR is a spectroscopic technique that was used to study the magnetic fields that are usually around atomic nuclei. These magnetic fields give details about the electronic structure of the molecule and the different functional groups present. This was used together with the FTIR for confirmation of the formation of functional groups

Figure 22: Bruker Ascend 500 Nuclear Magnetic Resonance Spectrometer from University of Johannesburg, Faculty of science. Supplied by Bruker, United States of America.

3.4.4. Rheology

Rheology was used to study of deformation, flow and viscosity of fluid materials under applied stress over time and a certain temperature range.

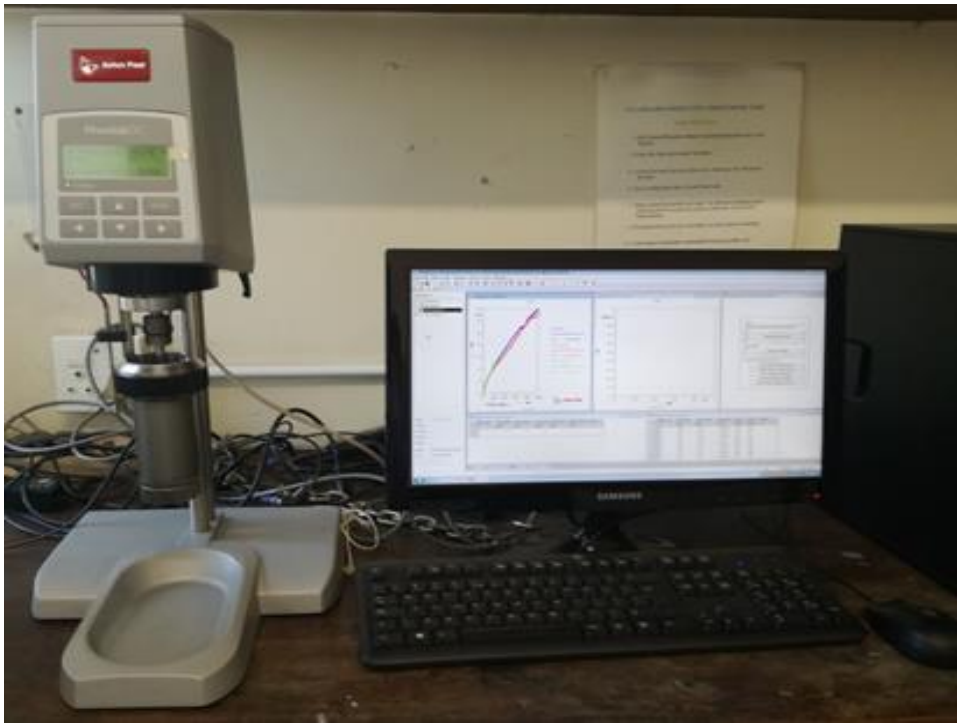

Figure 23: Image of a Rotational rheometer: RheolabQC from Wits - School of Chemical and Metallurgical Engineering. Supplied by Anton Paar, Austria

Chapter 4. Results and Discussions

4.1. Castor oil extraction

4.1.1. Castor Oil Extraction

Castor oil used in this investigation was extracted from the castor seed donated from Sedibeng Sa Dimelana (SSD), South Africa. The oil was extracted using the soxhlet set up as illustrated below in Figure 24. The process was conducted at a temperature of 80 °C to yield the castor oil. Firstly, the seeds undergo mechanical pressing, this was done by crushing the seeds to remove the shell. The moisture of the seeds was adjusted by placing the seeds in the oven. The following step was to place the crushed seeds into a hydraulic press and the seeds were pressed until they became cake-like to extract the oil. The oil in the cake was the recovered using the extraction method whereby heptane, hexane and petroleum ethers were used as solvents as during the Soxhlet extraction (Razdi, 2012).

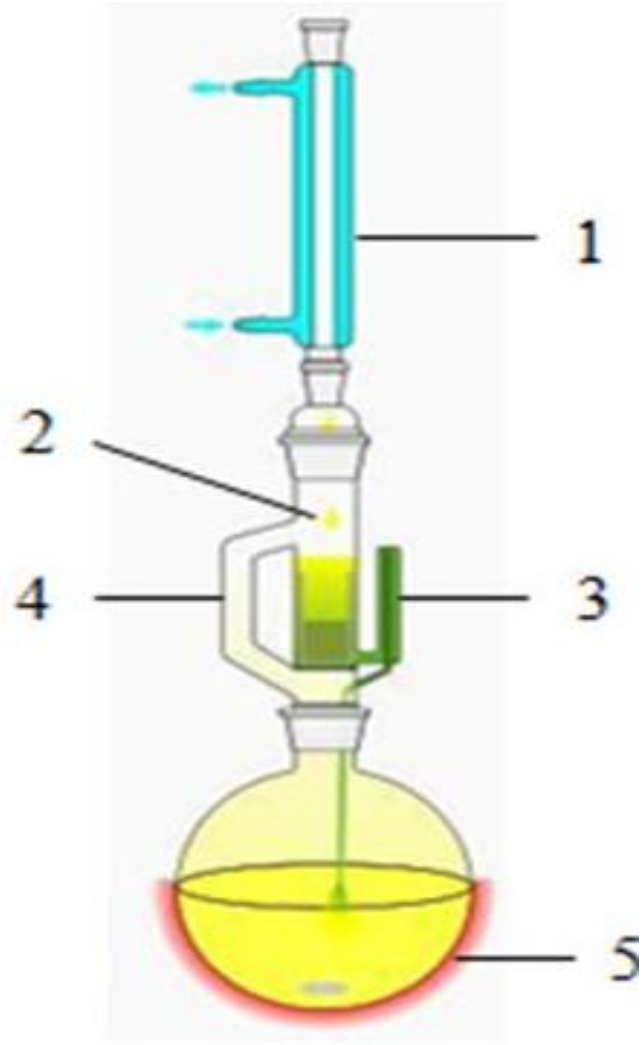

Figure 24: Soxhlet set-up where 1: condenser tube; 2: extraction tube with castor seeds; 3: siphon tube (with castor oil); 4: connection tube; 5: extraction flask. (Ji et al., 2017)

4.1.2. Characterization of castor oil

The castor oil that was extracted from the castor seeds supplied by SSD using the Soxhlet extraction was done to ensure that the oil had the properties of castor oil as outlined in the literature review. The total percentage of oil that was extracted from the castor seeds was 40%.

4.1.2.1. Fourier transform infrared spectrometry (FTIR)

Figure 25 is the Fourier transform infrared (FTIR) spectrum of the castor oil that was extracted for this study. The FTIR shows that the broad peak at 3415 cm^{-1} represents the OH bonds that are present in the castor oil. The stretch peaks at 2924 cm^{-1} and 2854 cm^{-1} represent the presence of the C-H bonds. The C=C bonds are observed at 1743 cm^{-1} and the 1458 bond represents the C=O bonds (Yang et al., 2017).

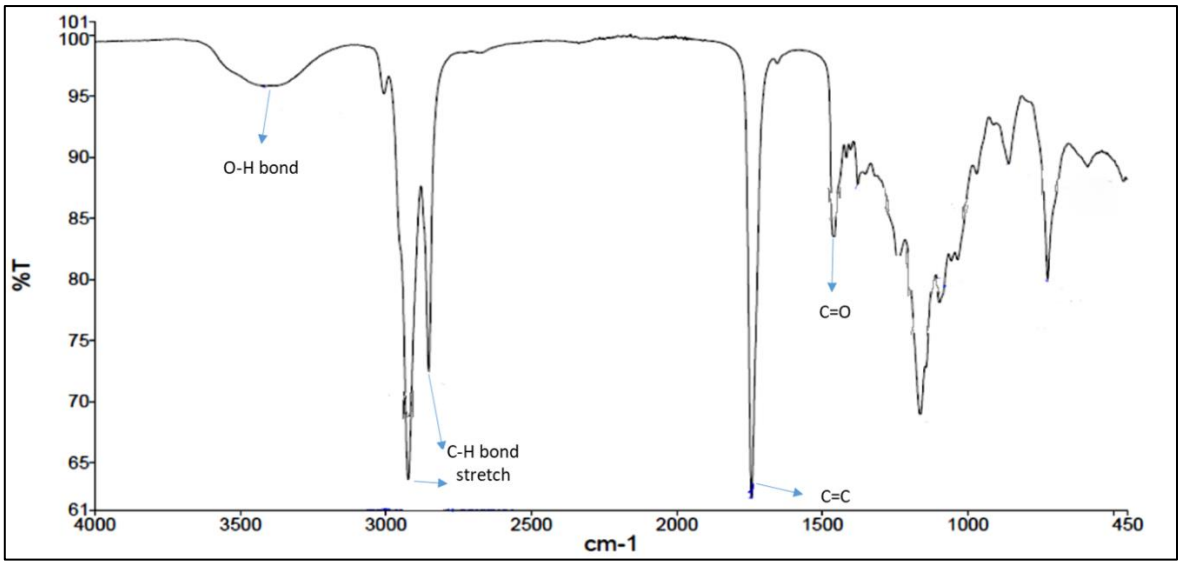

Figure 25: FTIR spectrum of castor oil

4.1.2.2. Nuclear Magnetic Resonance (NMR) spectroscopy

The NMR that was conducted for castor oil shows that there is a tertiary proton if the -CH_2CHCH_2- backbone that represents the vinyl protons structure at 5.4 – 5.7 ppm. The glycerol proton are seen at 5.2 – 5.3 ppm. The methylene proton appears at 4.1 – 4.3 ppm representing the -CH_2-$CHCH_2$-backbone. There is also a hydrogen adjacent to the hydroxyl proton in the fatty acid chain appears between 3.5–3.6 ppm. This is illustrated in Figure 26 aligns with the findings of (Zhang et al., 2015).

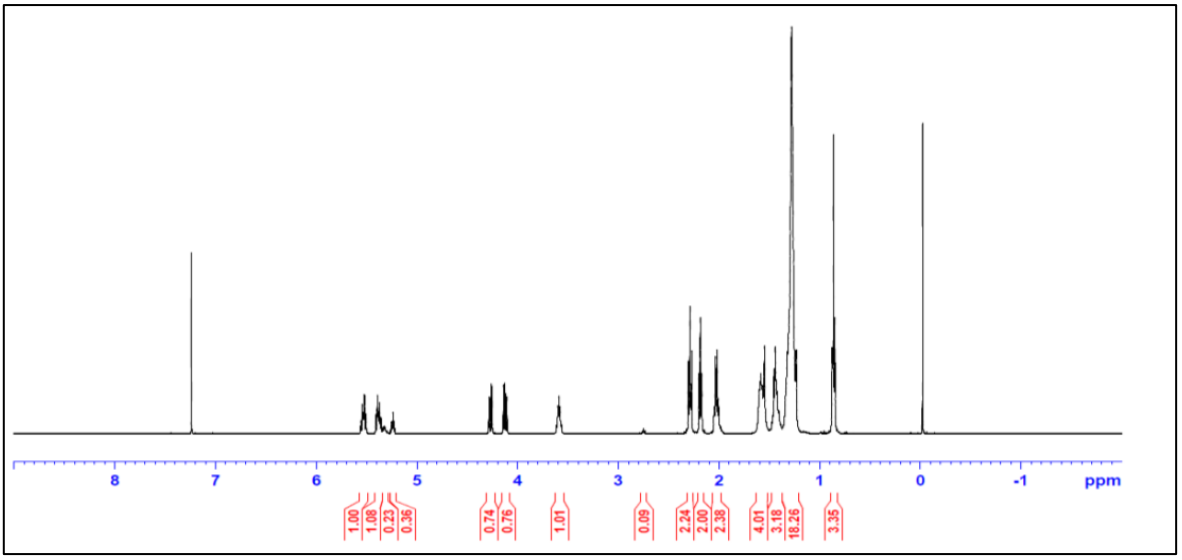

Figure 26: MNR Spectrum of castor oil

4.1.2.3. The rheology of castor oil

The deformation and viscosities of the castor oil were determined using rheology. The Newtonian or the Non-Newtonian behaviour of castor oil at temperatures 0 – 60 °C and the viscosity measured up to 900 cP at 0°C. The rheology studies of the castor oil extracted from the castor seed obtained from SSD illustrates that the viscosity of the castor oil decreases with increasing temperature (Figure 28), meaning that the higher the temperature, the easier it is for the castor oil to flow because of the effect of temperature in decreasing the hydrogen bond strength, as reported by (Abdelraziq & Nierat, 2015). The viscosity obtained in this investigation at 40°C was 240 cP, whereas literature has reported 231 cP (Neelamegam & Krishnaraj, 2011) and 271 cP (Robert, 1979), respectively.

The rheological study of castor oil has illustrated that the viscosity decreases with increasing shear rate as seen in Figure 28, meaning that castor oil undergoes shear-thinning. However the castor oil also behaves as a dilatant liquid when stress is applied whereby it thickens due to the increase in shear stress with increasing shear rate as illustrated in Figure 29 (Abdelraziq & Nierat, 2016).

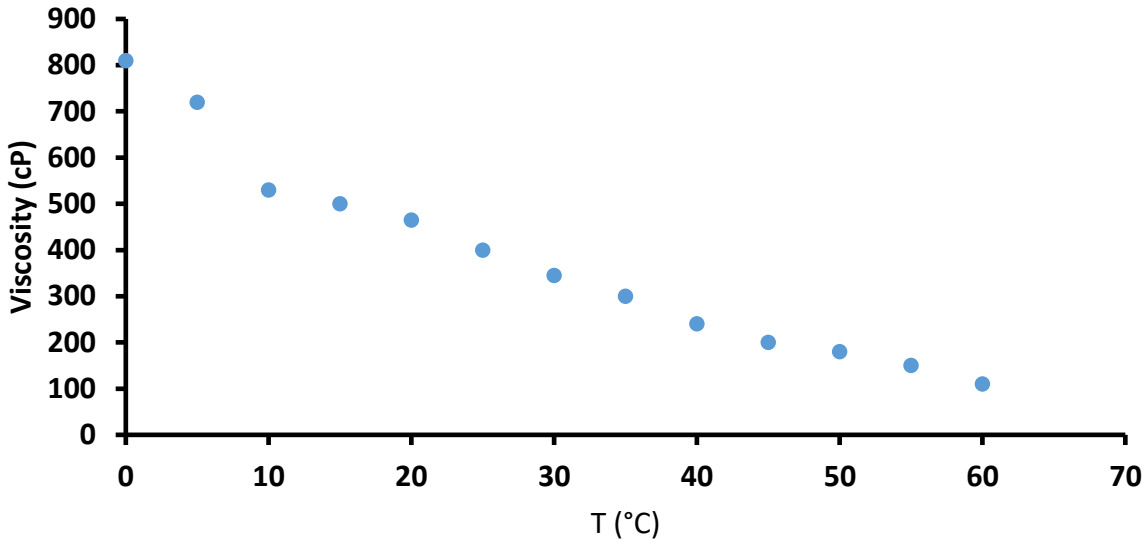

Figure 27: Viscosity of castor oil as a function of temperature

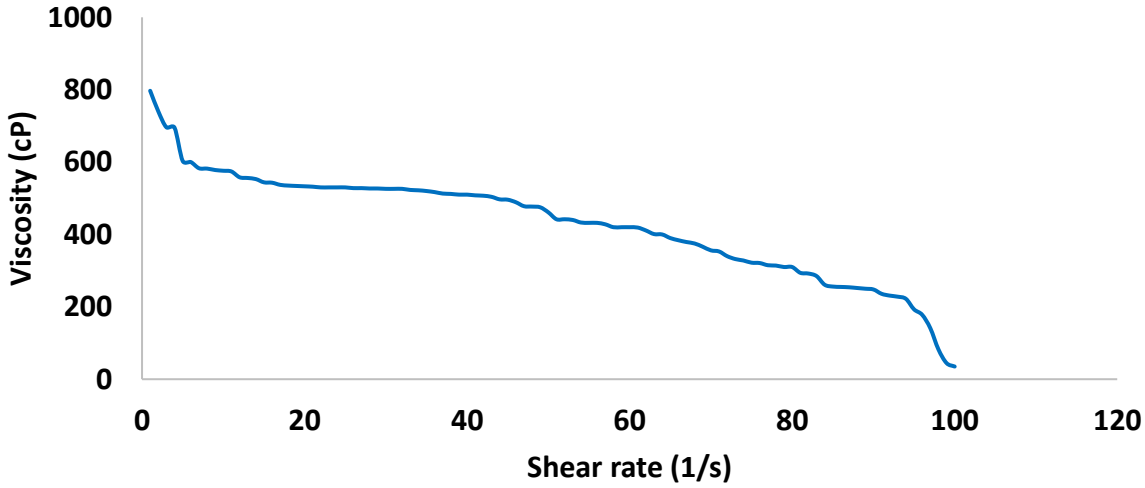

Figure 28: Viscosity of castor oil as a function of shear rate

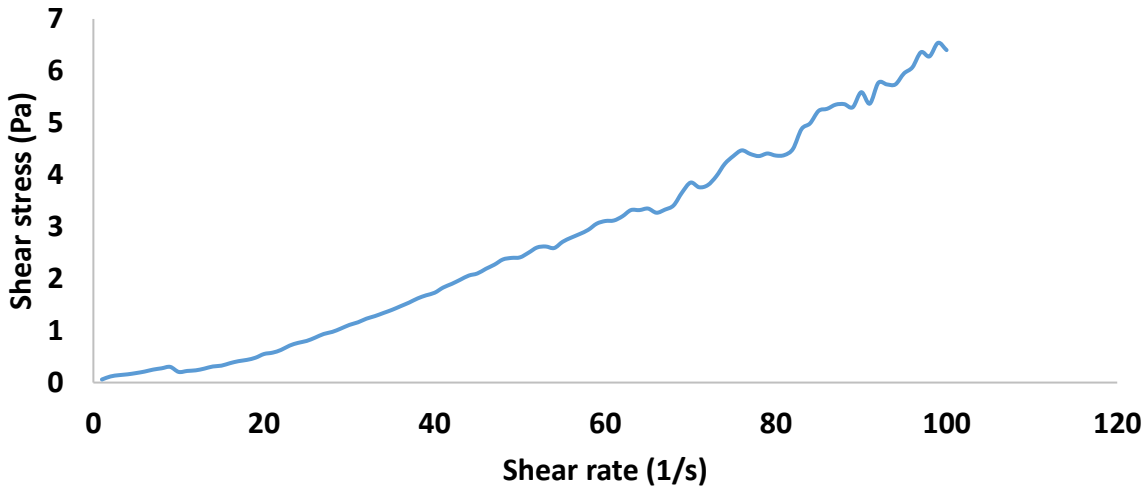

Figure 29: Shear stress of the castor oil as a function of shear rate

4.1.2. Thermal gravimetric analysis (TGA)

The TGA of the castor oil was conducted from 0 – 600 °C. The loss of mass of the castor oil is due to the thermal processes that comprises of cracking, decarboxylation, and the C–C bond cleavage. The mass losses were observed at 310 °C, 340°C, 460°C and 480°C; and the masses observed at these temperature points were 98%, 95%, 35% and 2.4%, with the final mass of 1.04% is detected at 480 °C. From 480 °C, there is no further mass loss detected, the TGA becomes almost flat from 480 – 600 °C as seen in figure 30. According to literature, the final mass residue that is detected is approximately 4 % in weight; therefore this can mean that the castor oil probably had more volatile materials than that used in literature (Li et al., 2017).

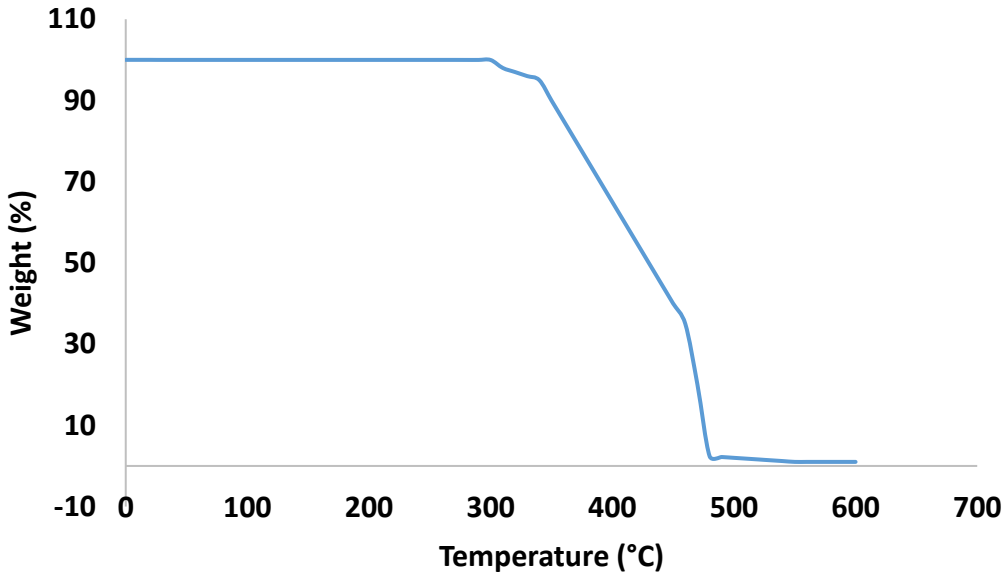

Figure 30: TGA analysis with the weight of castor oil as a function of temperature

4.2 Polycondensation Process

Figures 31, 32 and 33 show the synthesis of the HECA from the triglycerides and the amines, giving off the glycerol as the by-product. The HECA is then used for the second step of the synthesis to synthesize the CPEA, whereby again, the CPEA is then further synthesized to form the binder. From the initial procedure of 3 hours reaction time, the hours for the synthesis of the binder were varied from 1 to 4 hours to see if the reaction can be completed at a lesser time to save energy and also to see if an extra hour will give a more pure product after reaction.

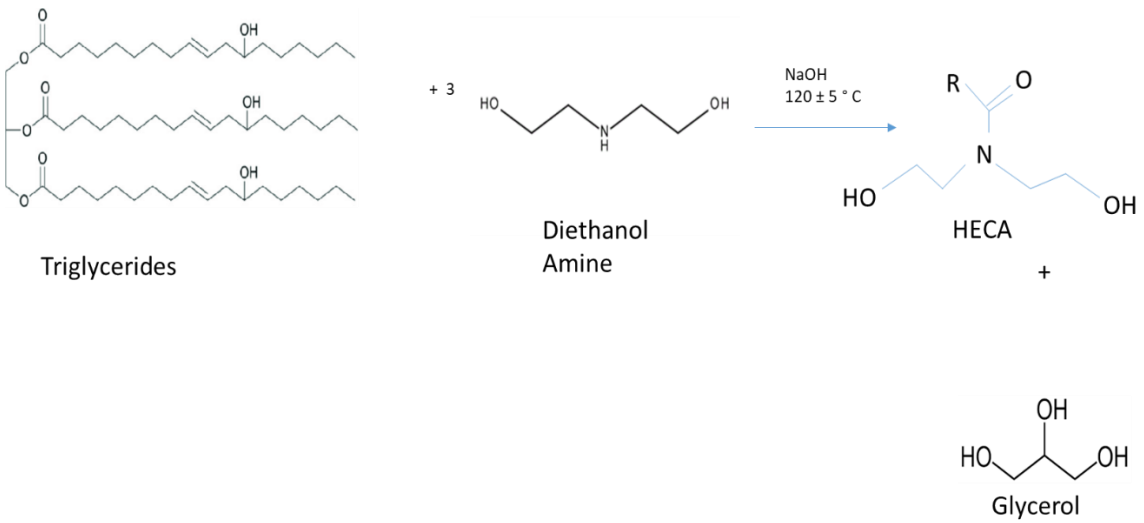

Figure 31: Synthesis mechanism of the HECA

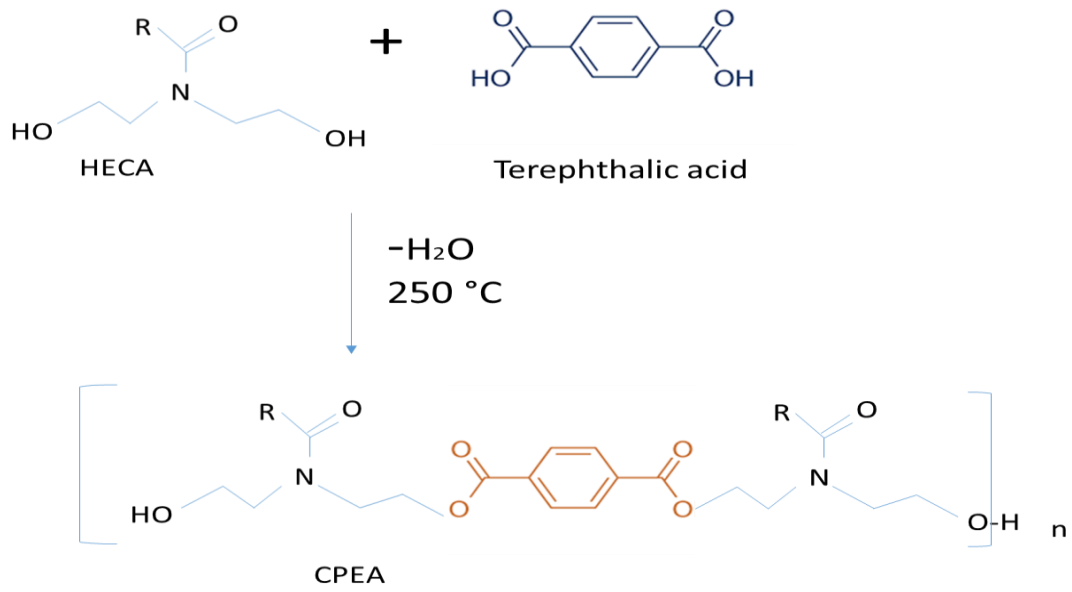

Figure 32: Synthesis mechanism of the CPEA

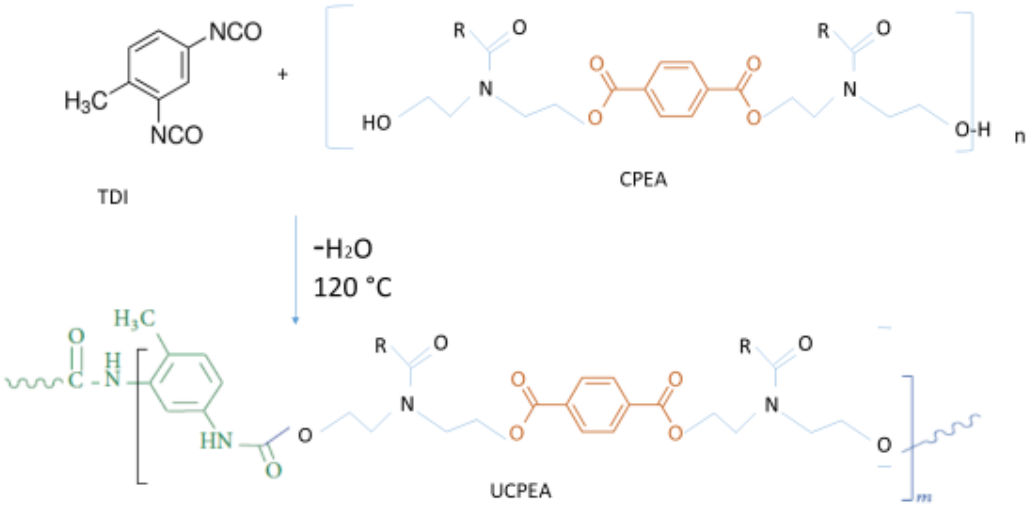

Figure 33: Synthesis mechanism of the UCPEA

4.2.1. FT-IR analysis results

The FTIR spectra was conducted for the three-step process of polycondensation, with the wavenumber ranging from 450 – 4000 cm^{-1}. The yields of the products are 60% HECA, 40% CPEA and 35% UCPEA.The comparison of the three spectra of HECA, CPEA, and UCPEA (binder) are shown in Figure 34. The FTIR spectrum of the HECA shows a distinctive broader band of hydroxyl group appearing at 3400 cm^{-1} as compared to the hydroxyl bands of the CPEA and the UCPEA. The methyl group (–CH_2–) symmetrical and asymmetric stretching occurs at 2906 and 2858 cm^{-1}. The amide carbonyl bands and C–N stretching bands appear at 1622 cm^{-1}, 1415 cm^{-1} (Ibrahim et al., 2015).

In the CPEA spectrum, the intensity of the hydroxyl broad-band has decreased as compared to that of the HECA at 3371 cm^{-1}. The additional band at 1774 cm^{-1} represents the carbonyl ester group. The aromatic ring from the terephthalic acid are represented by the peak that appear at 1478 cm^{-1} (Vieira da Cunha et al., 2004)

The spectrum of UCPEA observed additional bands that appear at 1734 cm^{-1} representing urethane linkages, and also 2970, 1465, 1413, and 771 cm^{-1} for –CH=CH–, aromatic ring of terephthalic acid and residual hydroxyl group which has lesser intensity at 3350 cm^{-1}.

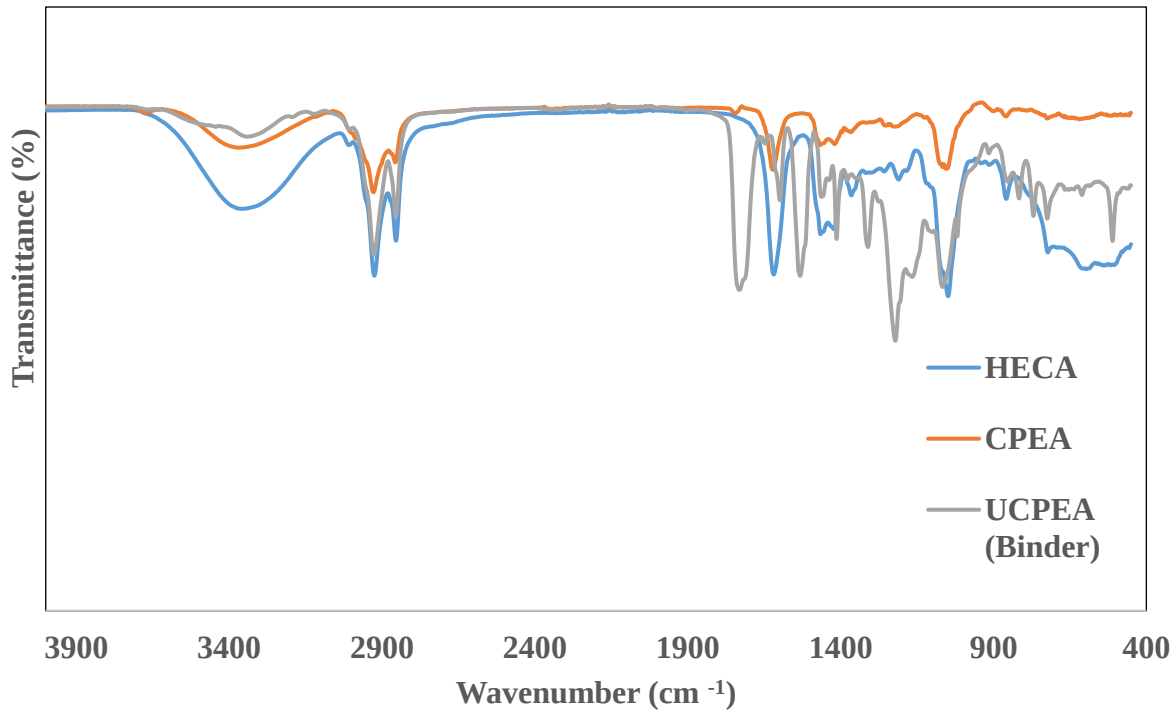

Figure 34: FTIR spectra of the three-step process of polycondensation, comparing the HECA, CPEA and the binder.

The FTIR spectra was conducted for the UCPEA synthesised with the variation in time from 1 and 4 hours. The comparison of the four spectra of UCPEA (binder) are shown in Figure 34 and they illustrate that the distinctive broad band of hydroxyl group appearing at 3361 cm^{-1} is more intense for the binder that was produced in 2 hours as compared to the other times in hours. The methyl group (–CH2–) symmetrical and asymmetric stretching occurs at 2927 and 2854 cm^{-1}, these peaks are more pronounced for the binders that were produced at 1 hour and at 2 hours. The amide carbonyl bands and C–N stretching bands appear at 1618 cm^{-1}, 1459 cm^{-1}; and these peaks are available for all the binders. There is also an additional stretch band at 1722 for the 1 hour binder that represents the urethane linkages (Vieira da Cunha et al., 2004).

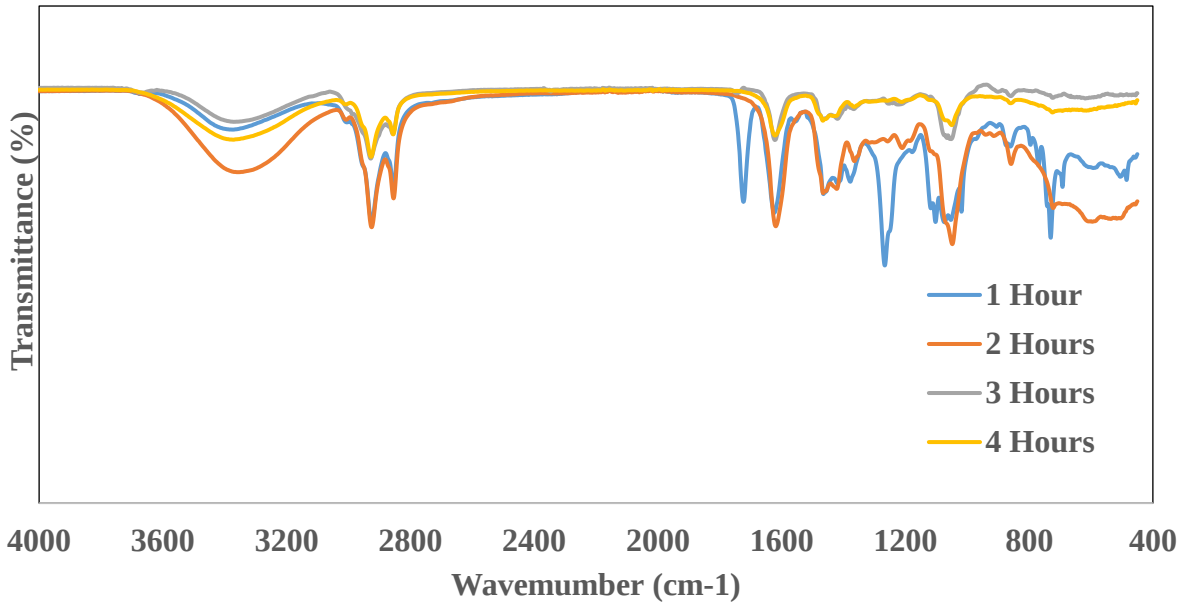

Figure 35: FTIR of the binder synthesized at different time intervals.

4.2.2. Rheology results of polycondensation process product

The deformation and viscosities of the UCPEA were determined using rheology. The Newtonian or the Non-Newtonian behaviour of UCPEAs at temperatures 0 – 100 °C and the viscosity measured to 900 cP at 0°C. The rheology studies of the UCPEAs that were synthesised using the same parameters and the only variation being the reaction time that ranged from 1 -4 hours. The viscosity of the UCPEAs decreases with an increase in shear rate as shown in Figure 36; where the viscosity of the UCPEA at 2 hours drops to 130 cP at 40°C; which is the lowest compared to others that drop to 521 (1 hour UCPEA), 275 (3 hours UCPEA) and 521 (4 hours UCPEA) at 40°C (Chen et al., 2016)

With the viscosities decreasing with increasing shear rate, this means that the UCPEAs undergo shear-thinning. However, the UCPEA also behaves as a dilatant liquid when stress is applied whereby it thickens due to the increase in shear stress with increasing shear rate as illustrated in Figure 37 (Chen et al., 2016).

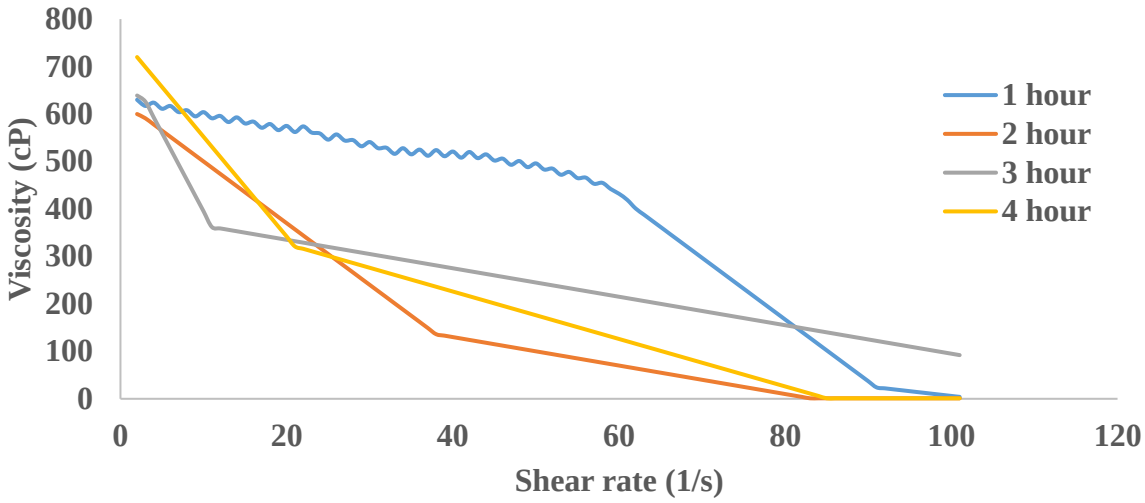

Figure 36: Graph illustrating the viscosity of the UPCEAs at different hours as a function of shear rate

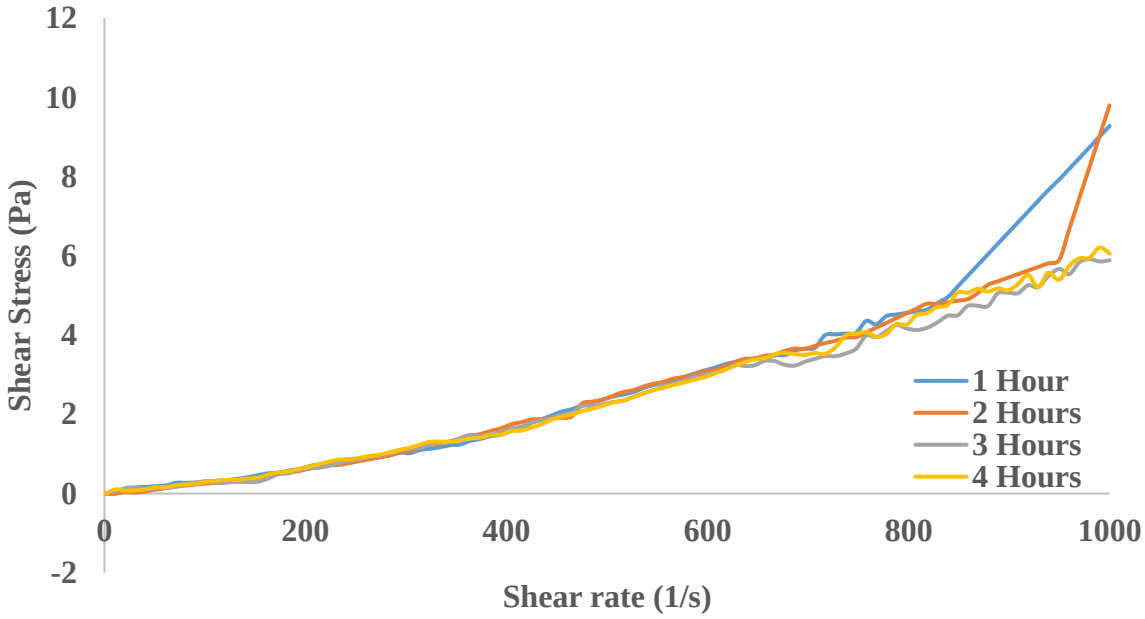

Figure 37: Graph illustrating the shear stress of the UPCEAs at different hours as a function of shear rate

4.2.3. TGA analysis results of polycondensation process product

The thermogram of the UCPEAs that were synthesized with varying times is illustrated below in Figure 38. The first minimal degradation of the polymer started around 50°C due to the presence of volatile compounds resulting in 90% weight. From then onwards, there is a continuous degradation at 340°C, 420°C, 425°C, 450°C, and 500°C; with the weight also decreasing from 83%, 80%, 50%, 30% and 2% . The UCPEA that was synthesized for 2 hours starts degrading at 410 – 600 °C and the results weight loss is 2.4 %, which is above the other resultant weights. In vegetable oil-based polyurethanes, generally, degradation starts after 150 °C, due to the degradation of urethane moieties; however, here the first step decomposition starts after 330 °C with the final mass at 4% (Kunduru et al., 2015).

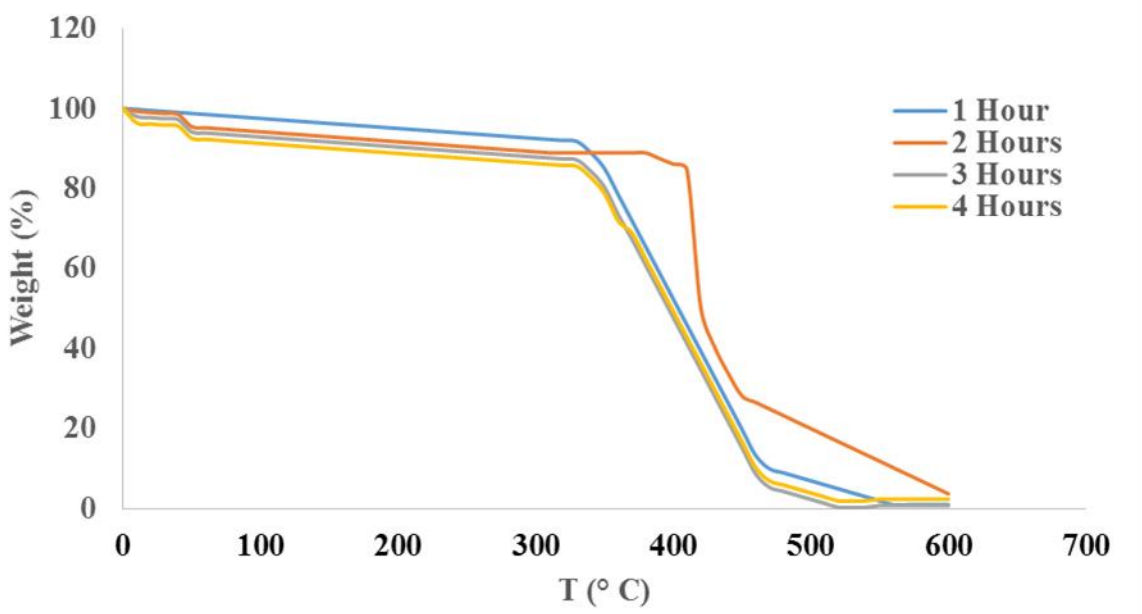

Figure 38: TGA analysis of the weight loss of UCPEA as a function of temperature

4.3. Epoxidation process

The epoxidation process followed the mechanism stated below resulting in a white product. The amount of the castor oil was varied from 5 – 20 wt.%. This was done because initially, the

synthesis of the binder was not reaching completion and only small amounts of the binder would be obtained. The increase was to see if more binder can be produced by increasing the castor oil and keeping the catalyst amount constant.

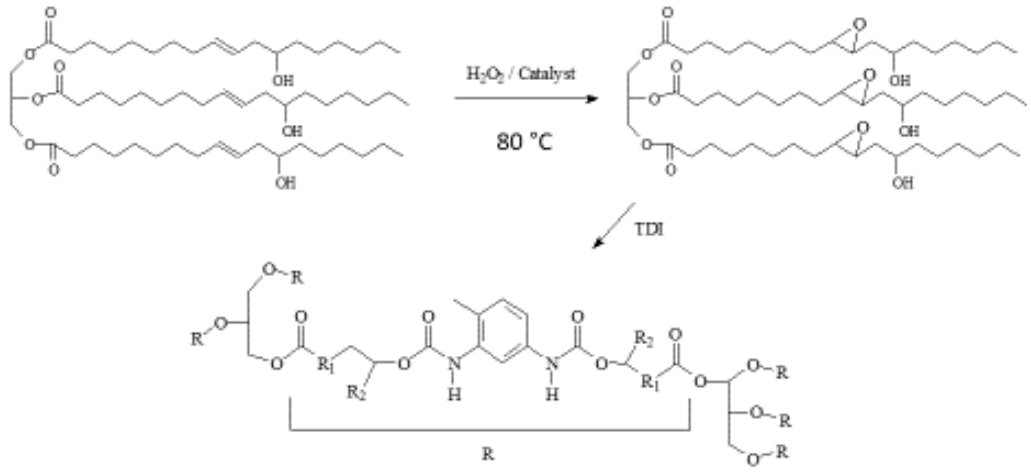

Figure 39: Synthesis mechanism of the epoxidation process

4.3.1. FTIR of the Epoxidation Catalyst (M)

Before the epoxidation of the castor oil was conducted for the synthesis of the polyurethane, a catalyst was first synthesized and below (Figure 40) is the FTIR spectrum of the catalyst that is known as catalyst M. The FTIR of the catalyst was conducted at a wavenumber ranging from 400 – 4000 cm^{-1}. The spectrum of the catalyst illustrates that there is a very small peak of the hydroxyl group appearing at 3662 cm^{-1}. The methyl group (–CH2–) symmetrical and asymmetric stretching occurs at 2922 and 2853 cm^{-1}. The amide carbonyl bands and C–N stretching bands appear at 1634 cm^{-1} and 1487 cm^{-1} respectively (Abi Munajad et al., 2018).

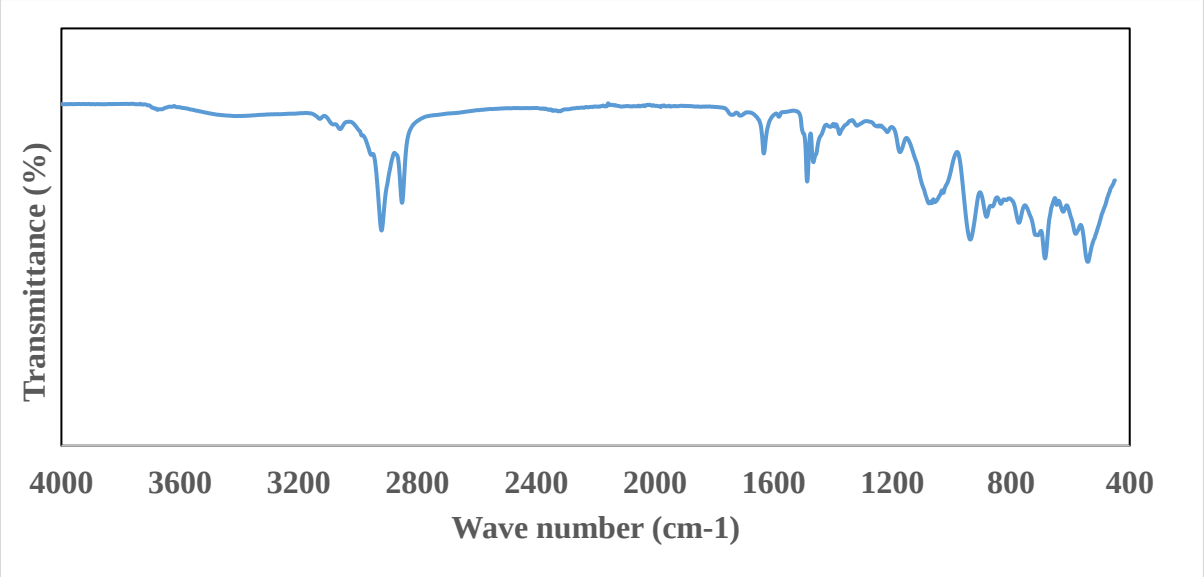

Figure 40: FTIR spectrum of the epoxidation catalyst

4.3.2. FTIR Spectroscopy results of the epoxidized castor oil-based bio binder

The FTIR spectrum of the epoxidized castor oil-based bio-binder is illustrated in Figure 41. In the FTIR spectrum of the epoxidized castor oil binder, there is a peak that appears at 3376 cm^{-1} which represents the O-H bond and axial deformation. The CH_3 stretch peak is observed at 2930 cm^{-1}. The peak of ester carbonyl was observed at 1623 cm^{-1}. Other distinctive peaks that represent the formation of the epoxy group [-(C-O-C-)-], can be observed at 1052 cm^{-1} and 862 cm^{-1}. The other peaks are possible probably due to the interference of the peaks of other moieties (Parada et al., 2016). This synthesis method has proved to be more consistent and shows ideal repeatability though the amounts of castor oil were varied.

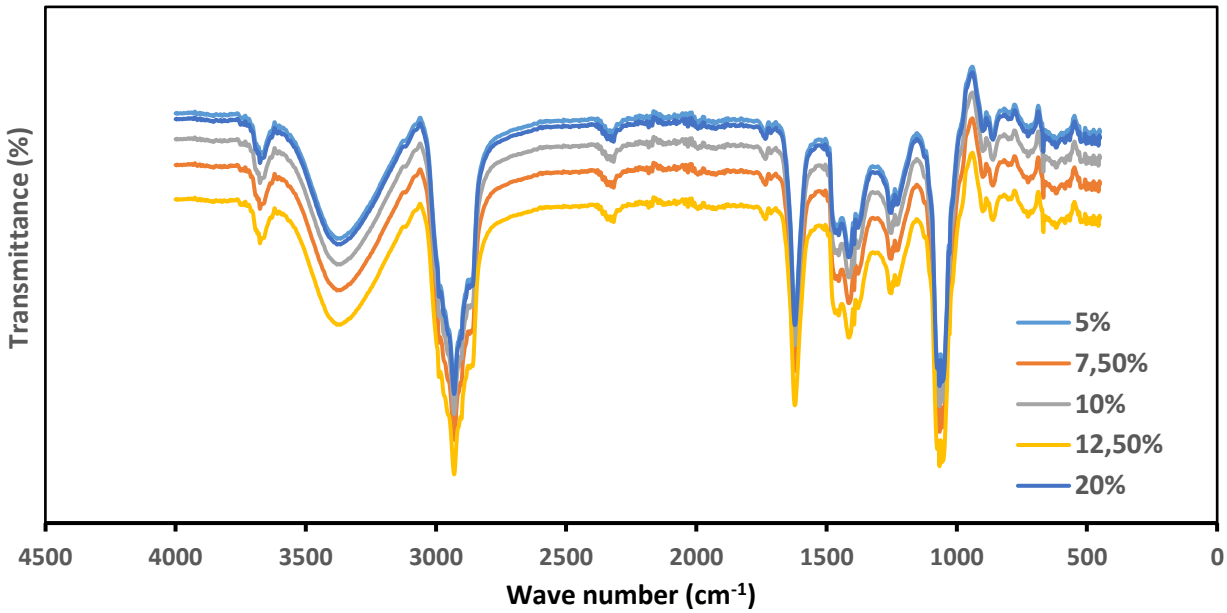

Figure 41: FTIR spectrum of the binders formed from epoxidation of the castor oil

4.3.3. Rheology of the epoxidized castor oil based bio binder

The deformation and viscosities of the epoxidized castor oil based bio binder were determined using rheology. The Newtonian or the Non-Newtonian behaviour of binders was determined at temperatures 0 – 100 °C and the viscosity measured to 900 cP. The rheology studies of the binders that were synthesised using the same parameters and the only variation being the weight percentage (5 – 20 wt. %) of the castor oil loading. The viscosity of the polymers decreases with an increase in shear rate as shown in Figure 42; where the viscosity of the polymers with 5 wt. % decrease less as compared to the other polymers.

With the viscosities decreasing with increasing shear rate, this means that the polyols undergo shear-thinning. However, the binders also behaves as a dilatant liquid when stress is applied whereby it thickens due to the increase in shear stress with increasing shear rate as illustrated in Figure 43.

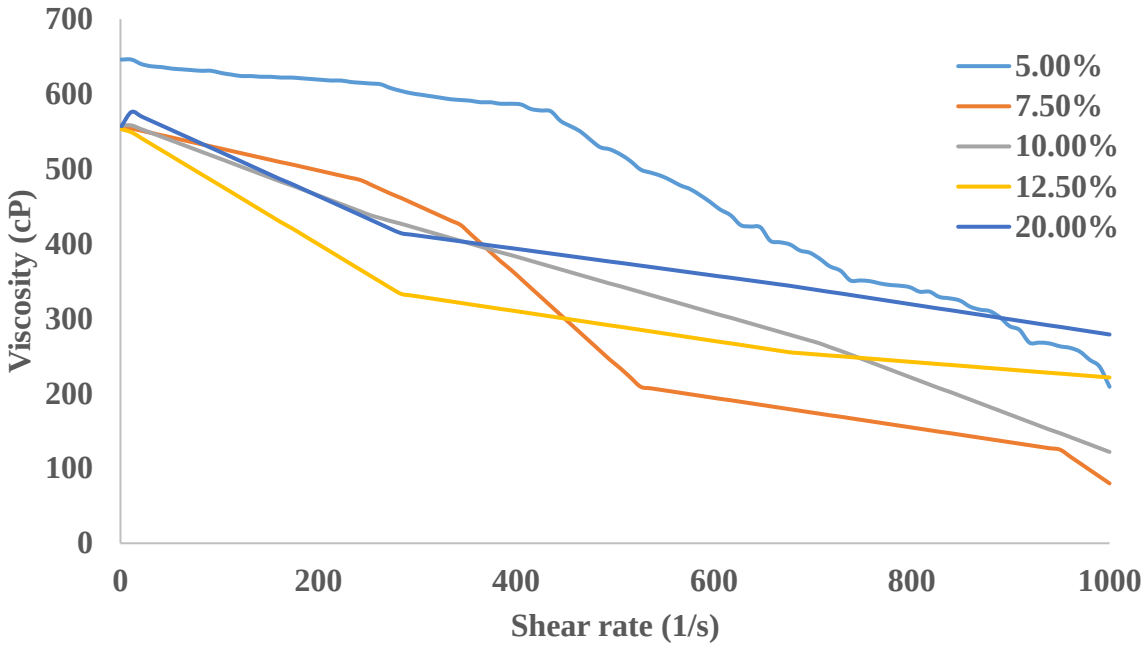

Figure 42: Graph illustrating the viscosity of the epoxidized castor oil-based bio binders with varying castor oil loading as a function of shear rate

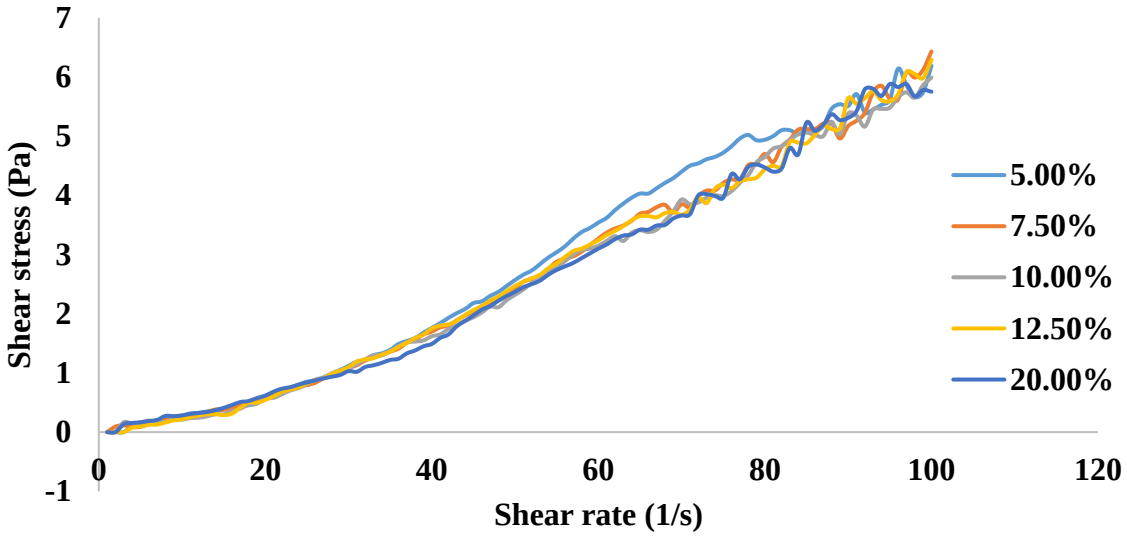

Figure 43: Graph illustrating the shear stress of the epoxidized castor oil based bio binders with varying castor oil loading as a function of shear rate

4.3.4. Thermogravimetric analysis (TGA) epoxidized castor oil based bio binders

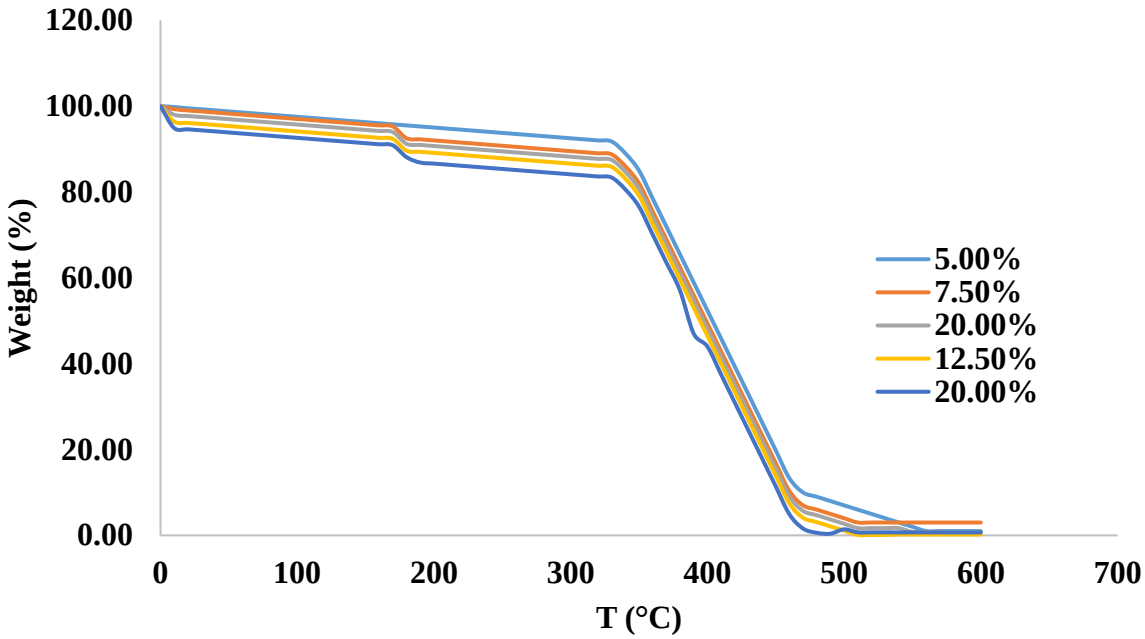

Figure 44: TGA analysis of the weight loss of epoxidized castor oil based bio binders as a function of temperature

The TGA of epoxidized castor oil based bio binders is illustrated in Figure 44. As shown in Figure 44, all of the binders, excluding the binder with 5 wt. %, were thermally stable in nitrogen atmosphere below 170 °C and exhibited a two-stage thermal degradation process that occurs in the subsequent heating. The first stage (about 170 – 330 °C) and second stage that is visible in all binders including the 5 wt.% binder that hardly decomposed at first; at about 340 – 470 °C is more complex due to cross linking containing C=C bond. The process of thermal degradation of polyenes involves the molecular chain C-C bond breaking to form small molecules, meanwhile, aromatization produces aromatic compounds, and these aromatic compounds undergo further thermal degradation.

4.4. Ozonolysis process

The ozonolysis process as illustrated in figure 45 shows that O_3 was generated using an ozone generator that is connected to an oxygen cylinder. Because the amount of ozone that was introduced into the reaction could not be properly accounted for, the castor oil amount was then varied to get optimum conditions for the process.

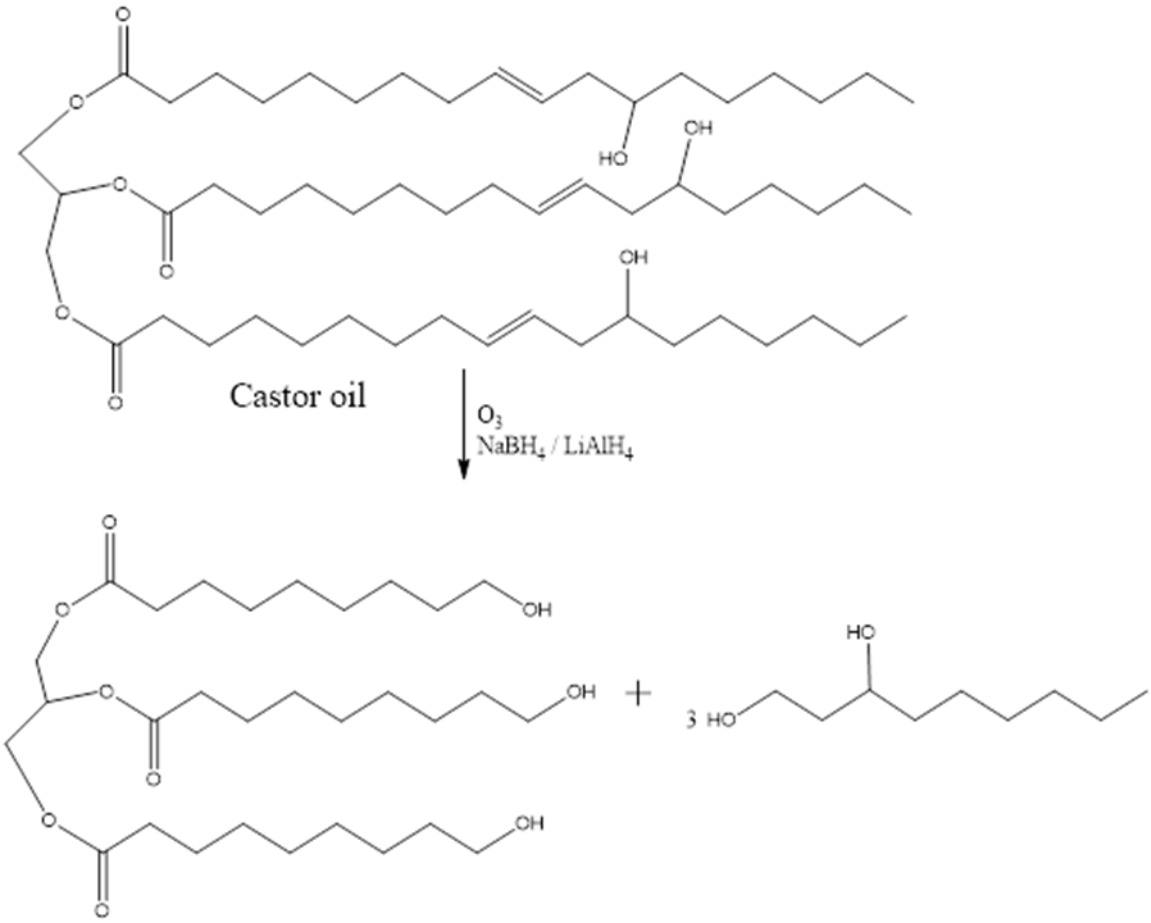

Figure 45: Synthesis mechanism of the epoxidation process

4.4.1. FTIR Spectroscopy results of the binders formed through ozonolysis

The polyols obtained from castor oil have the main peaks assigned to the triglyceride of 9-hydroxynonanoic acid. The FTIR as illustrated in Figure 46 show similar patterns of the different polyols. The hydroxyl broad-band is observed for all polyols at 3361 cm^{-1}. The methyl group (–CH_2–) symmetrical and asymmetric stretching occurs at 2927 and 2855 cm^{-1}. The amide carbonyl bands and C–N stretching bands appear at 1729 cm^{-1} and 1464 cm^{-1} respectively; and these peaks are available for all the binders (Cvetkovic, et al., 2008). There

are additional C=C peaks for the 40 wt.% containing polyol, this is probably because most of the castor oil was still in the reaction and did not go to completion. The peak that represents the ozo group is also available at 1269 and 875 cm^{-1}.

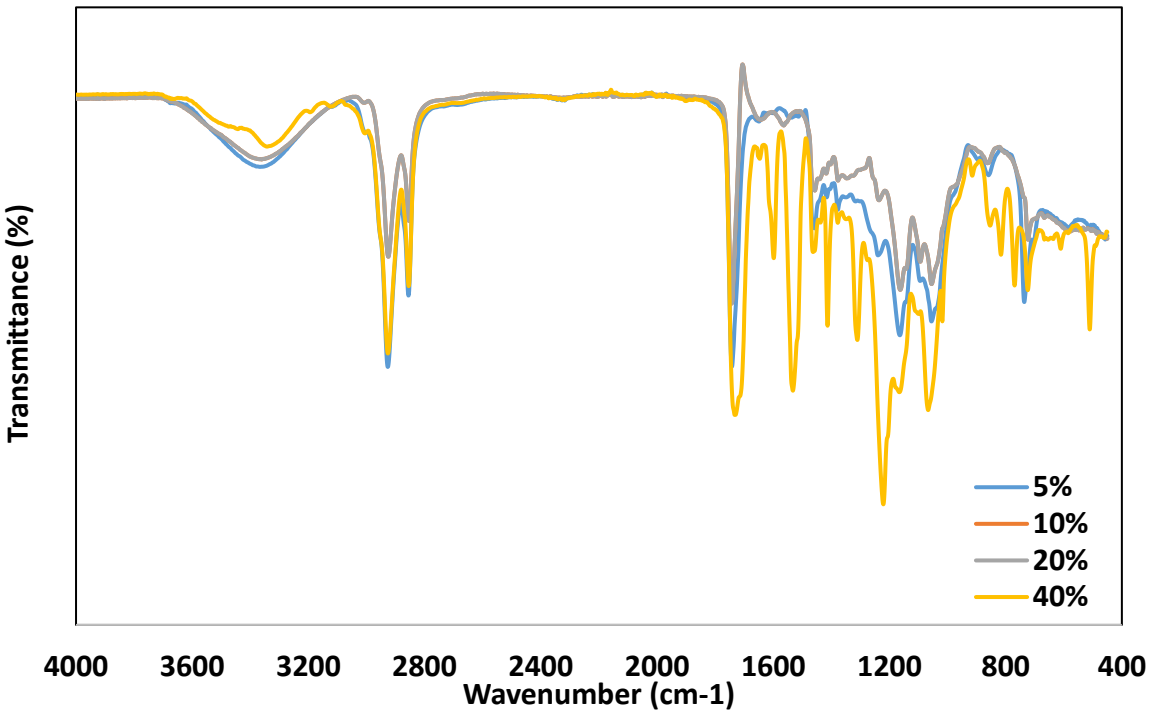

Figure 46: FTIR spectrum of the polyurathanes (binders) formed from ozonolysis of the castor oil with different amounts of the castor oil

4.4.2. Rheology results of the binders formed through ozonolysis

The deformation and viscosities of the ozonolysis castor oil based bio binder were determined using rheology. The Newtonian or the Non-Newtonian behaviour of polymers at temperatures 0 – 100 °C and the viscosity measured to 900 cP. The rheology studies of the polymers that were synthesised using the same parameters and the only variation being the castor oil loading (5 – 40 wt. %). The viscosity of the polymers decreases with an increase in shear rate as shown in Figure 47; where the viscosity of the polymer with 40 wt.% of castor oil takes longer to decrease viscosity as illustrated in Figure 47 (Gao et al., 2018).

With the viscosities decreasing with increasing shear rate, this means that the polyols undergo shear-thinning. However, the binders also behaves as a dilatant liquid when stress is applied whereby it thickens due to the increase in shear stress with increasing shear rate as illustrated in Figure 48.

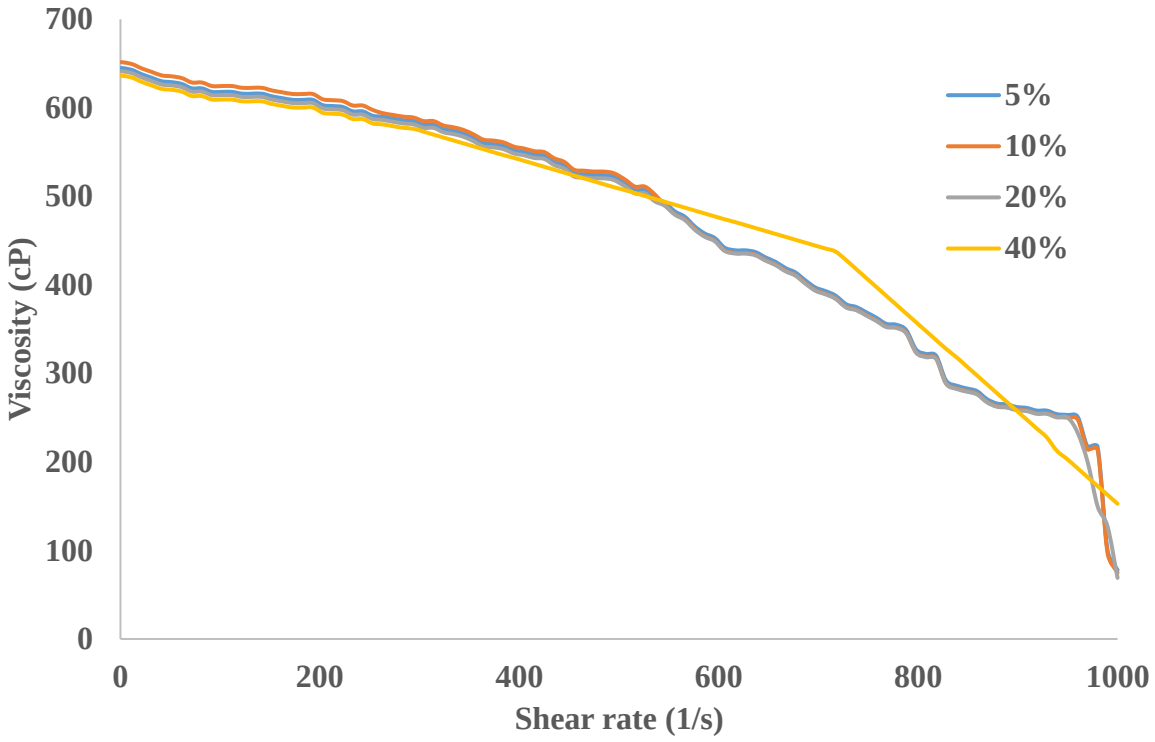

Figure 47: Graph illustrating the viscosity of the ozo-castor oil-based bio binders with varying castor oil loading as a function of shear rate

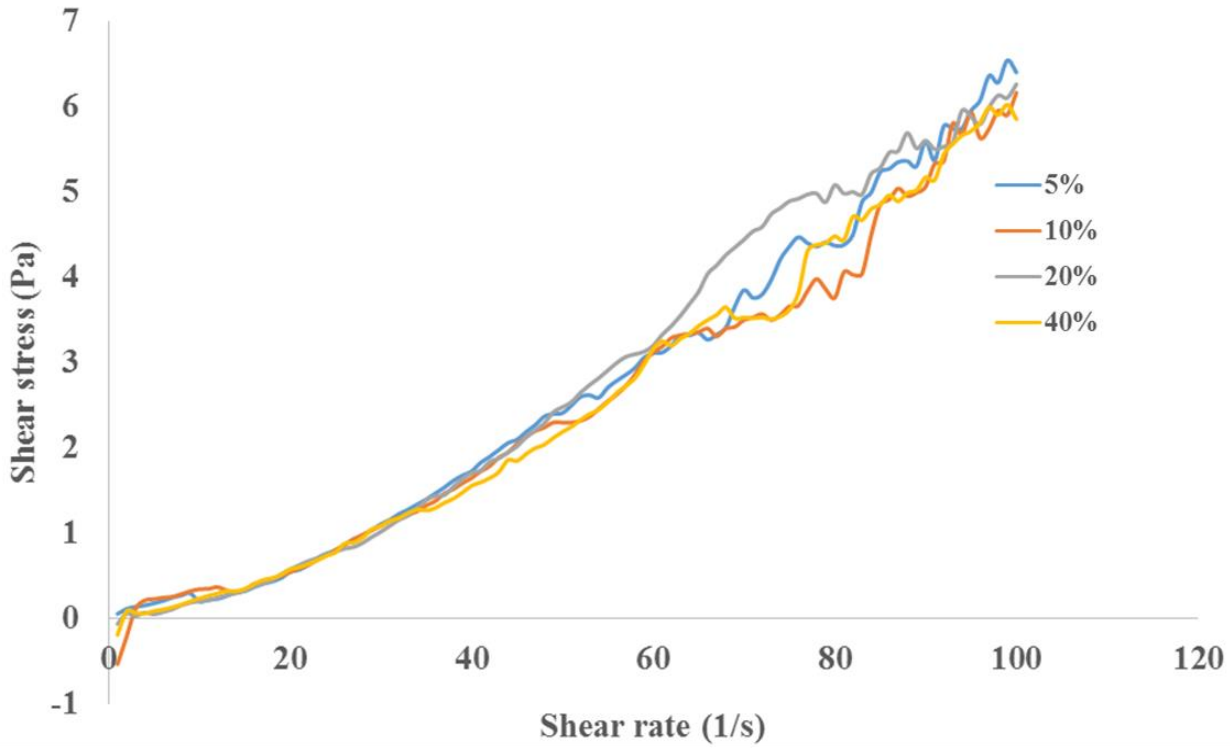

Figure 48: Graph illustrating the shear stress of the ozo-castor oil based bio binders with varying castor oil loading as a function of shear rate

4.4.3. Thermogravimetric analysis (TGA) of the ozo-castor oil based bio binders

The TGA of epoxidized castor oil-based bio binders is illustrated in Figure 49. As shown in Figure 49, all of the binders, excluding the binder with 5 wt. %, were thermally stable in nitrogen atmosphere below 340 °C and exhibited a two-stage thermal degradation process that occurs in the subsequent heating. The first stage (about 340– 390 °C) and second stage that is visible in all binders including the 5 wt.% binder that hardly decomposed at first; at about 390 – 470 °C is more complex due to cross-linking containing C=C bond. The process of thermal degradation of polyenes involves the molecular chain C-C bond breaking to form small molecules, meanwhile, aromatization produces aromatic compounds, and these aromatic compounds undergo further thermal degradation (Tenorio-Alfonso , et al., 2017).

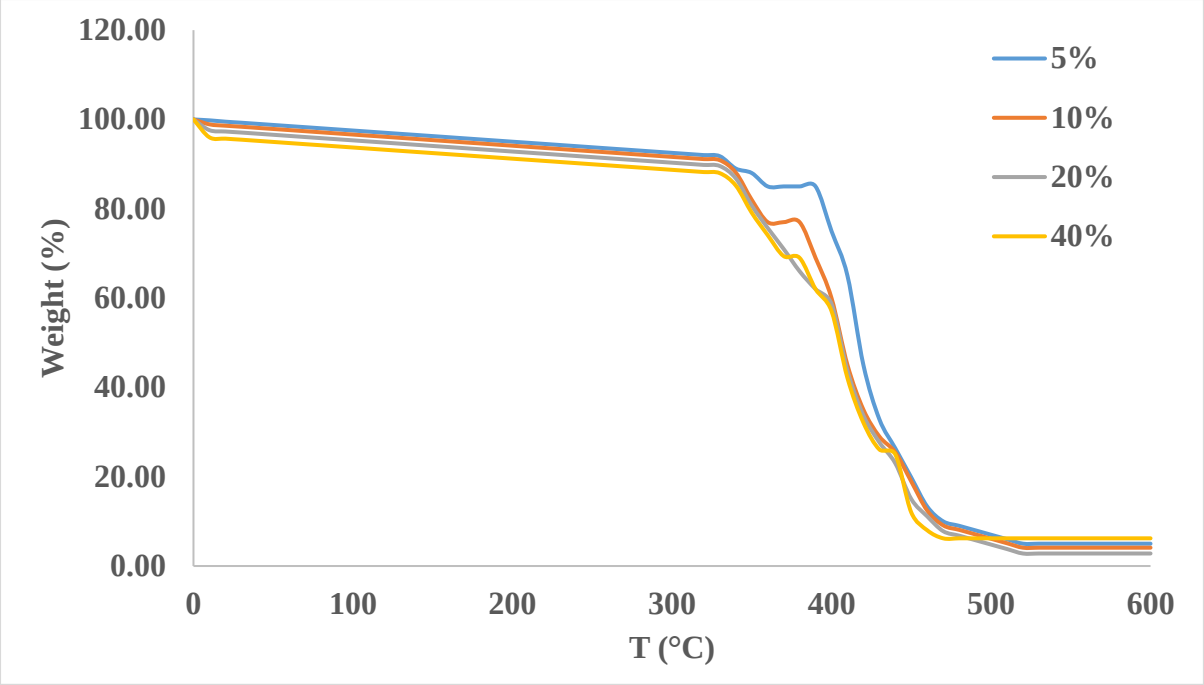

Figure 49: TGA analysis of the weight loss of ozo-castor oil based bio binders as a function of temperature

4.5. Summary of results

Table 7: Summary of the three processes

Parameters	Polycondensation	Epoxidation	Ozonolysis
Synthesis Temperature range (°C)	150 to 250	100 to 120	-40 to 110
Time (Hours)	2	3	4
Decomposition Temperature (°C)	400	330	390
Viscosity Drop	Medium	fast	slow
Number of chemicals used	14	14	8
Number of steps	8	8	6
Reaction to total completion	no	no	no

Chapter 5: Conclusion and Recommendations

5.1 Conclusion

From the processes listed above, a process that uses less energy and does not result in many side reactions will be ideal. Castor oil is of benefit because it does not compete with edible oils and hence threatening food security. The various products that are obtained from castor oil have proved that the properties contained in the castor oil are worth exploring for various applications for the replacement of fossil fuel. The research objectives were met as from the FTIR and NMR spectra, the modified functional groups and the polymeric binder's monomer were identified.

The characterization results of SSD castor oil align with the expected protons of the HNMR spectrum and range of the rheology behaviour. The viscosity profile relates the decreased in hydrogen bond strength with the increase in temperature. The spectrum of UCPEA produced through polycondensation confirmed the polyurethane product at the expected peak representing urethane linkages (1734 cm^{-1}), and also CH=CH– (2970, 1465, 1413, and 771 cm^{-1}). The UCPEA (binder) produced in 2 hours showed distinctive viscosity behaviour and broad band of hydroxyl group appearing at 3361 cm^{-1} of the FTIR spectrum, which is more intense compared to the investigated process times. The effect of castor oil content on the epoxidation and ozonolysis process showed that 5 % oil excess is sufficient to prepare a castor oil based binder.

The ozonolysis process is most recommended synthesis process based on the results obtained thus far though it is the longest process in terms of time as compared to epoxidation and polycondensation. Ozonolysis uses the least amount of temperature, reagents and processing steps making the process more energy and cost efficient.

In conclusion, the three methods were successfully selected for the development of the castor oil-based bio-binder. The methyl and the hydroxyl functional groups were successfully modified to enable the introduction of binder properties. Also, the produced monomers were polymerized and modified to produce the desired binder.

5.2 Recommendations

Due to the time constraint, it is recommended to investigate the effect of various parameters such as process temperature, stirring speed, reactants and/ or catalyst amount on the quality of the binder produced. It will also be interesting to investigate the kinetic behaviour of the ozonolysis and epoxidation processes.

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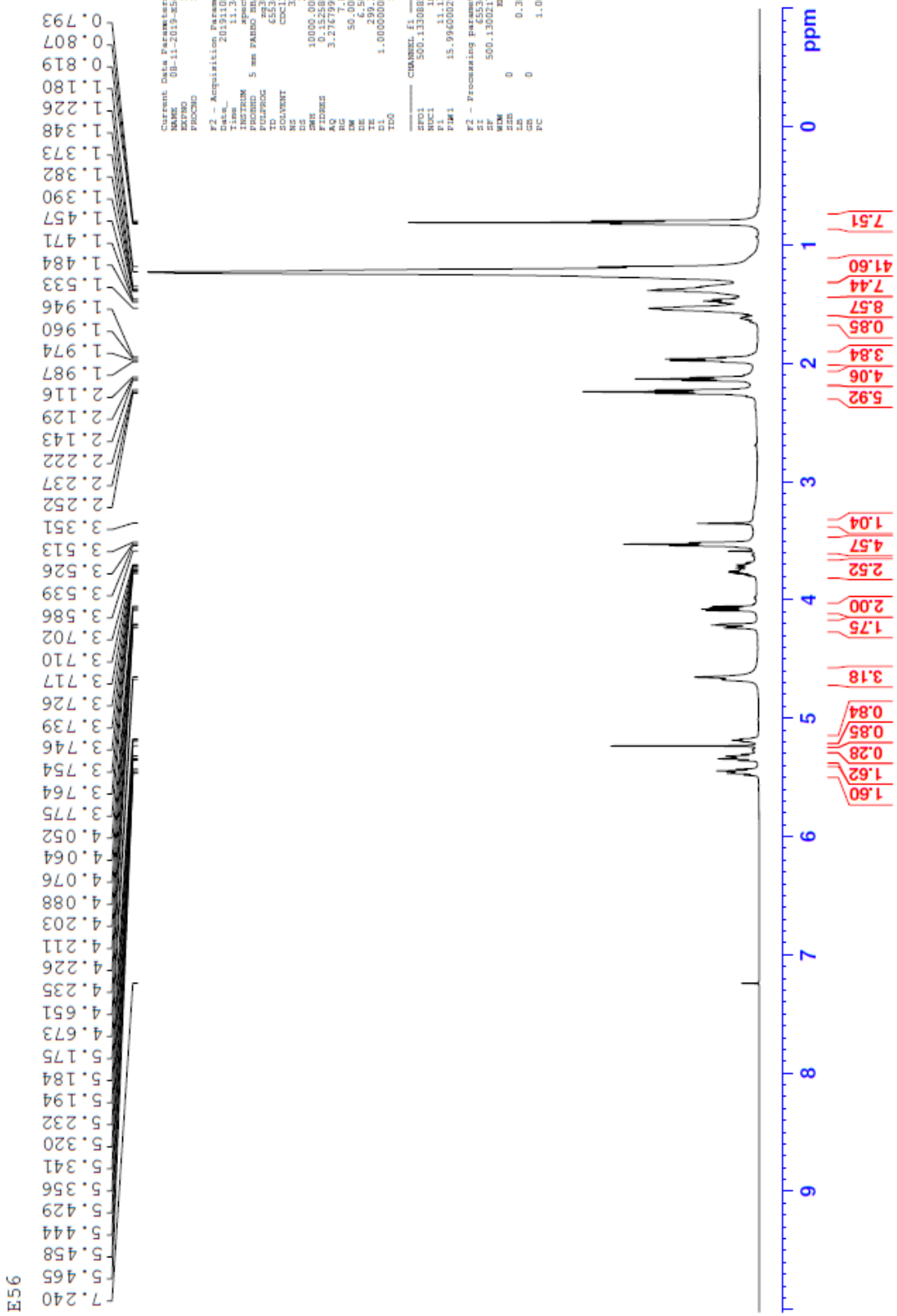
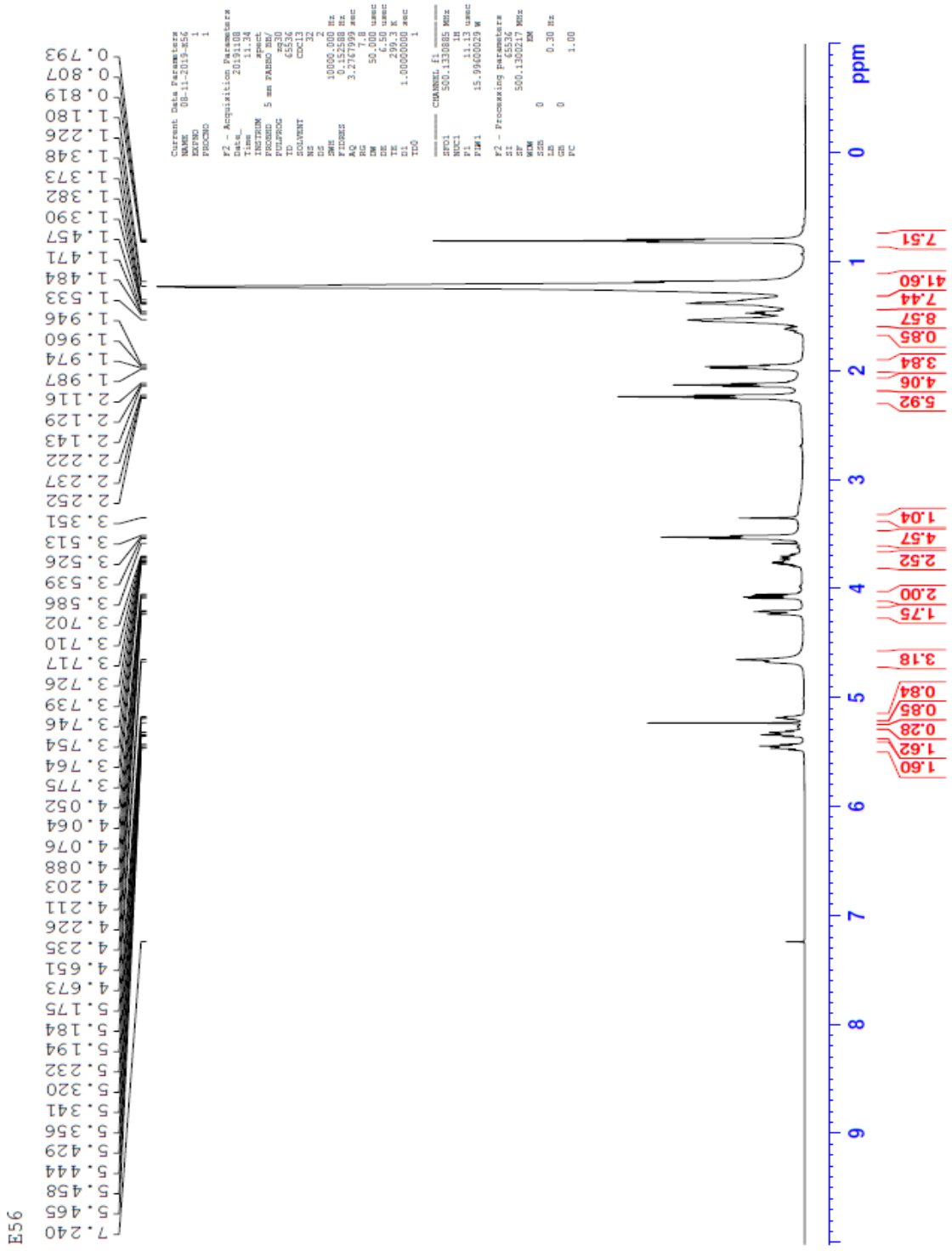
Appendix

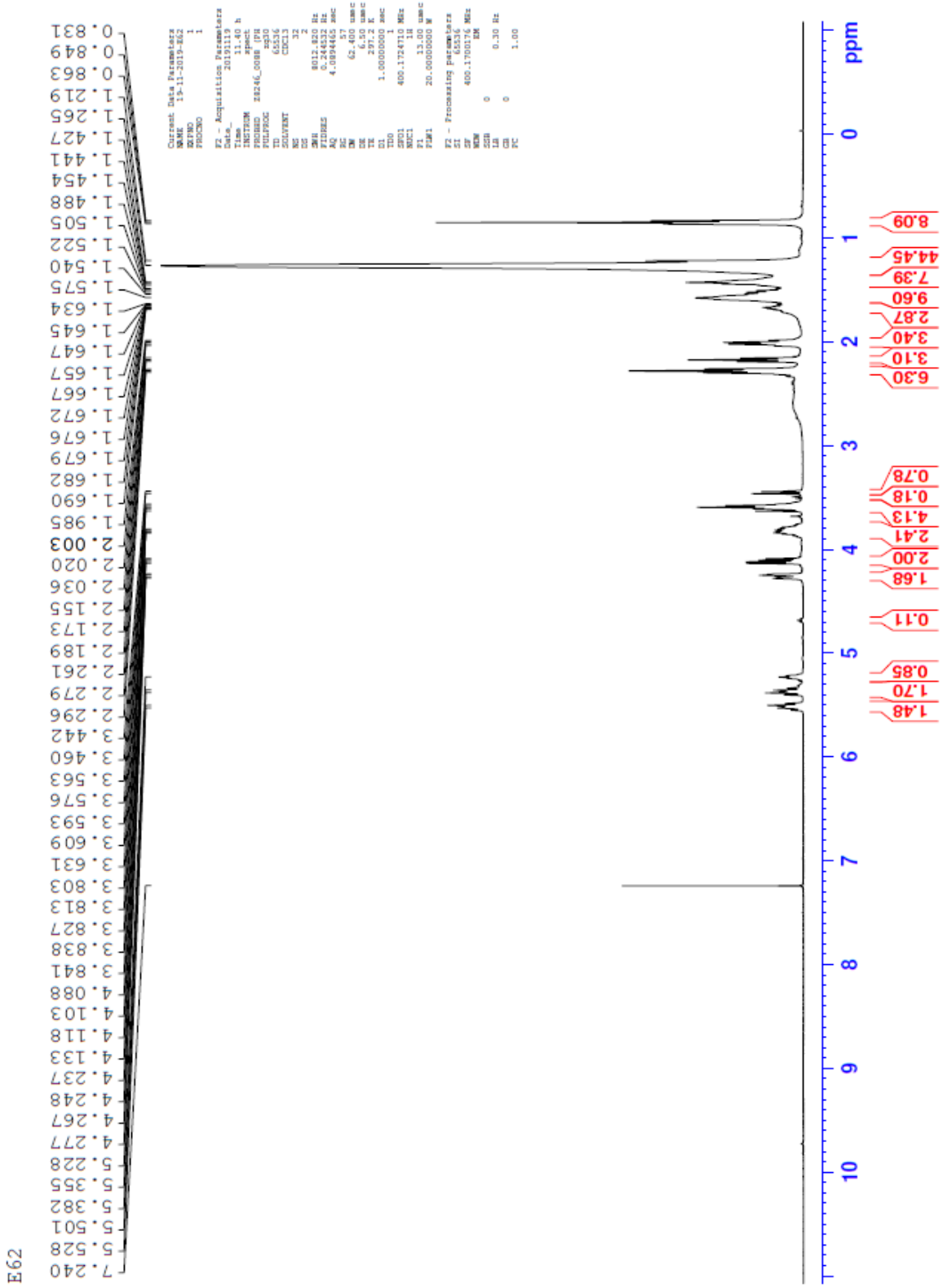
a. NMR of the ozonolysis process for 3 hours



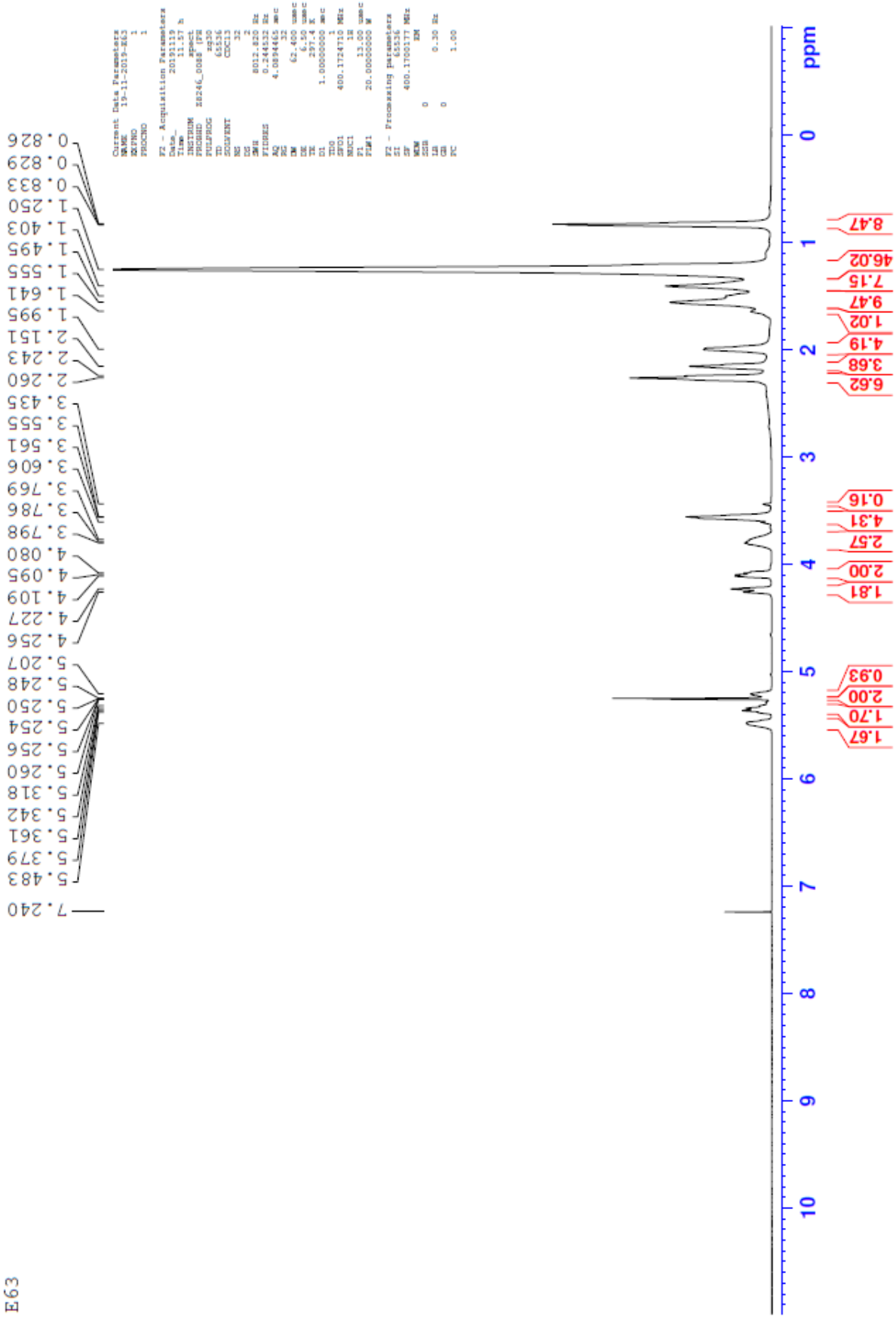
b. Repeat of the NMR of the initial ozonolysis process



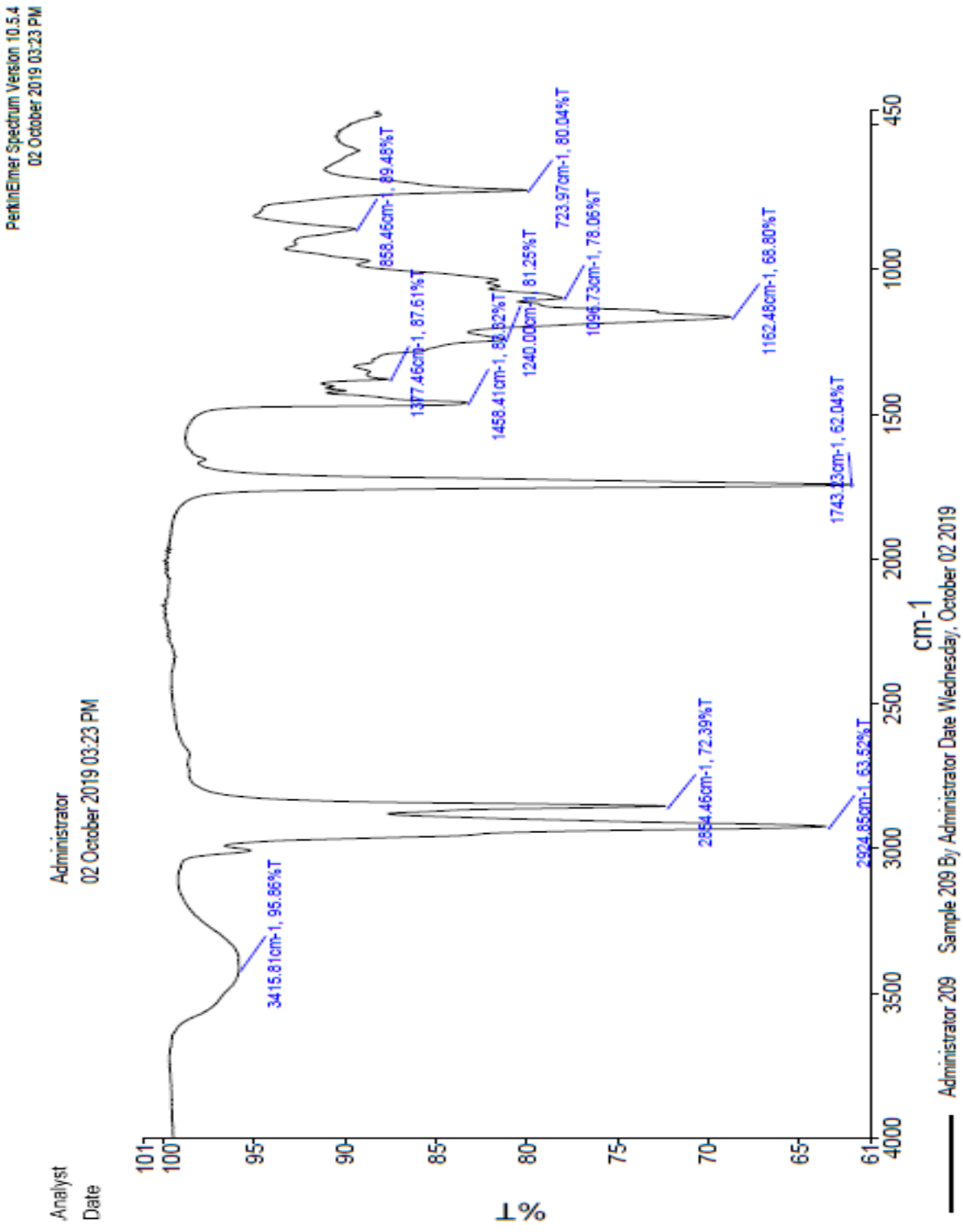
c. Repeat of the NMR of the ozonolysis process for 4 hours



d. Repeat of the NMR of the ozonolysis process for 4 hours repeat



e. FTIR of the ozonolysis process



f. Repeat FTIR of the ozonolysis process