SYNTHESIS OF POLYURETHANE FROM ONE HUNDRED PERCENT SUSTAINABLE NATURAL MATERIALS THROUGH NON-ISOCYANATE REACTIONS

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SYNTHESIS OF POLYURETHANE FROM ONE HUNDRED PERCENT SUSTAINABLE NATURAL MATERIALS THROUGH NON-ISOCYANATE REACTIONS

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GLOSSARY (SYMBOLS OR ABBREVIATIONS)

APES	3-aminopropyltriethoxysilane
ATR	Attenuated Total Reflectance
CDCL	Deuterated Chloroform
CSBO	Carbonated Soybean Oil
DMSO-d6	Deuterated Dimethyl Sulfoxide
EO	Ethylene Oxide
ESBO	Epoxidized Soybean Oil
FAO	Food and Agricultural Organization of the United Nations
FTIR	Fourier Transform Infrared Spectroscopy
HDI	Hexamethylene Diisocyanate
IPDI	Isophorone Diisocyanate
KBr	Potassium Bromide
MDI	Diphenylmethane Diisocyanate
NIPU	Non Isocyanate Polyurethane
PO	Propylene Oxide
TBAB	Tetrabutylammonium Bromide
TDI	Toluene Diisocyanate
THF	Tetrahydrofuran
USD	United States Dollar
v/v	volume/volume

SUMMARY

The synthesis route for the preparation of polyurethane using 100% sustainable materials was proposed. Lignin, one of the most abundance biomass on Earth, was used as one raw material, while the other one used is soybean oil. The reaction occurs in 3 steps, and is done in 2 different pot reactions. Briefly, purchased epoxidized soybean oil is carbonated to synthesize carbonated soybean oil. Then carbonated soybean oil was reacted with coupling agent, 3-aminopropyltriethoxysilane to produce urethane monomers. Finally, prepared urethane monomers were polymerized with lignin to produce sustainable polyurethane. Molecular structures were intensively analyzed using Fourier-Transform Infrared Spectroscopy and Nuclear Magnetic Resonance Spectroscopy. In addition, mechanical properties of prepared polyurethane were analyzed in order to evaluate its performance and compare with the polyurethanes available commercially. Our results indicated that the highest tensile strength achieved was 1.4 MPa, which is slightly below the typical tensile strengths of processible polyurethane. Chemical properties of all the intermediates and products and implications for future research are discussed.

1. Motivation and objectives

Synthetic polymers are becoming more and more essential for modern human life and are taking every part of our daily lives in order to keep it convenient and rich. However, most synthetic polymers have been developed from petroleum derived chemicals and they are not compatible with the environment since they cannot be part of natural recycling system and possess limited availability. Therefore, researchers nowadays are keen to replace petroleum chemicals with renewable resources to develop synthetic polymers. Nevertheless, the synthesis of polymeric materials from renewable resources still remains as one of the greatest challenge for the researchers. Therefore, development of environmentally friendly polymers is the key to not only sustainable society, but also to maintain our life rich and convenient.

The primary object of this study is to synthesize polyurethane from two different monomers derived from biomass and lignin and soybean oil were selected as raw materials. Although both of raw materials are found abundance in all parts of the world, only a small amount is currently utilized for the use of synthetic polymers. Therefore, it is important to accomplish valorization of these raw materials and its incorporation into polyurethane, which is one of the most widely used synthetic polymer, is a viable option among several possibilities. Chemistry and mechanism of the modification of each raw material have been studied intensively. Moreover, polyurethane from two different monomers has been successfully synthesized and its mechanical properties were characterized to address its performance and the effects of lignin contents have been investigated.

2. Introduction and Literature Review

2.1 Polyurethane

2.1.1 Current Polyurethane and Drawbacks

Polyurethane is any polymer consisting of a chain of organic units joined by urethane linkage (-NHCOO-). Polyurethane has quickly developed to be one of the most widely used polymer with a continuously increasing global market since its first lab synthesis in 1937. [1] As per Research and Markets, the global market for polyurethanes was estimated at 13,650.00 kilo tons in 2010 and is expected to increase to 17,946.20 kilo tons by 2016 with compound annual growth rate of 4.7% from 2011 to 2016. Moreover, the market was estimated to be $33,033 million USD in 2010 and is expected to achieve $55,479.68 million USD by 2016. The polyurethane market is mainly dominated by the furniture and interior industry, which accounts for 28.01% of the total demand, whereas the second largest use of polyurethane is in construction industry, which accounted for 24.98% of the overall market in 2010. [2]

Polyurethanes have been used in wide range of applications, such as construction, packaging, insulation, bedding, upholstery, footwear, vehicle parts, panting, etc. Polyurethanes occur the form of rigid, semi-rigid, flexible foams, elastomers, and high viscous liquid. Rigid polyurethanes foams can be mainly used as an insulating material in construction refrigeration applications, whereas flexible foams are primarily used as a cushioning material in the applications of transportation, furniture, packing, etc. Elastomers can exist in either thermosetting elastomers or thermoplastic elastomer. [3] Compared to conventional materials, such as wood and metals, polyurethane has its own unique merits, such as low density, low thermal conductivity and moisture permeability, a high strength to weight ratio and high dimensional stability. [4]

Furthermore, polyurethanes can be produced with desired properties for specific applications, by adjusting the formulation and reaction conditions of polyurethane synthesis and the use of additives. [5] Although polyurethane offers lots of benefits, it still has some drawbacks including poor degradability and toxicity due to the use of isocyanates which have motivated researchers to find more environmental friendly starting materials.

Conventional polyurethanes are usually synthesized through the polycondensation reaction between a diisocyanate and a diol. [6-8] (Figure 1) Diols are molecules that contain two hydroxyl groups. They can be prepared by base-catalyzed addition of propylene oxide (PO) or ethylene oxide (EO) onto a hydroxyl or amine containing initiator, or by polyesterification of a di-acid, such as adipic acid, with glycols. Diisocyanates are molecules that contain two isocyanates groups; it can be in aromatic form, such as diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI) or aliphatic form such as hexamethylene diisocyanate (HDI) or isophorone diisocyantate (IPDI). Of these, MDI and TDI are diisocyanates that are mostly used as the starting materials for polyurethanes. However, isocyanates are notably toxic chemical and synthesized from an even more toxic substance phosgene which causes environmental hazards. (Figure 2) Moreover, exposure to isocyanates can cause health effects, such skin irritation and long-term asthma. [9]

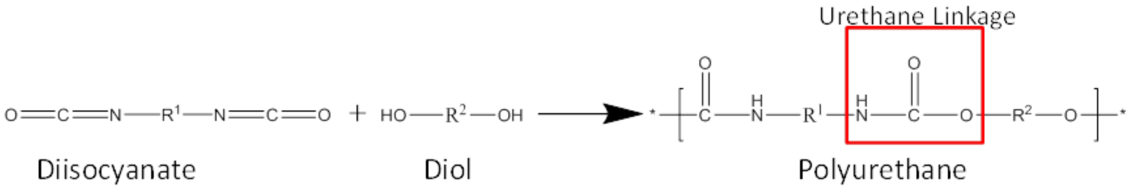


Figure 1 Conventional Synthesis of Polyurethane

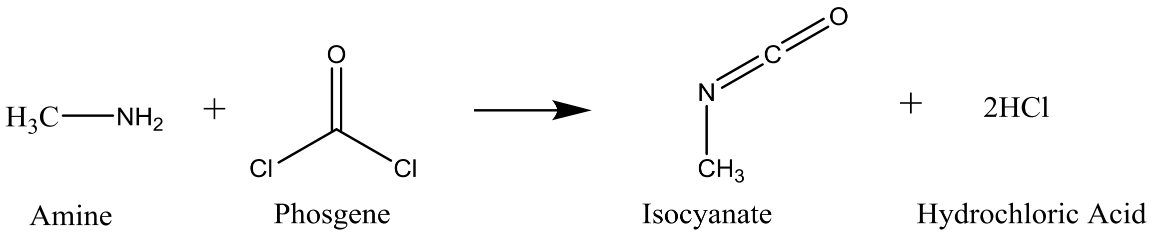


Figure 2 Synthesis of isocyanate using phosgene

During the process of moisture curing of polyurethane coatings, the reaction between isocyanate and water can be difficult to handle. Normally, the isocyanate can undergo an irreversible reaction with water, forming a urea and carbon dioxide, resulting in an unusable product. [10] (Figure 3) Therefore, extremely careful isolation of these materials from water is required until the coatings are applied to the surface.

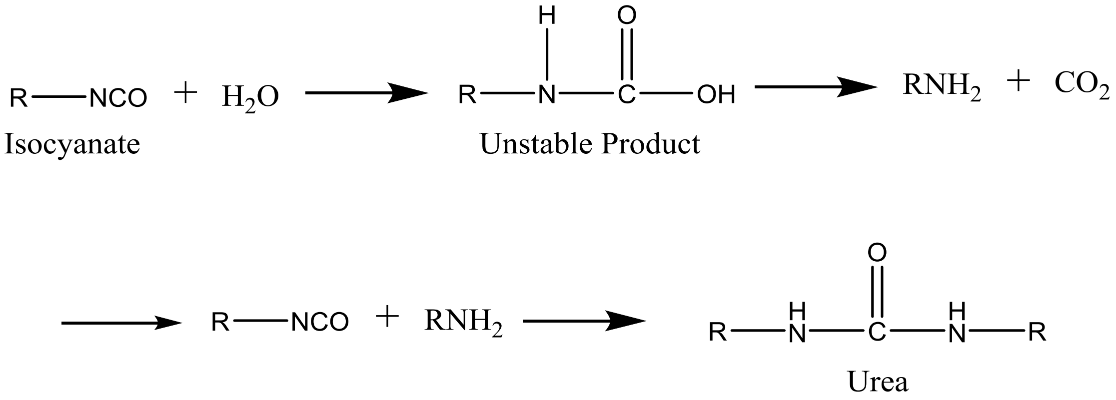


Figure 3 Reaction between isocyanate and water

Moreoever, conventional polyurethanes exhibit an inherent weakness in weatherability and poor chemical resistance in the back bone due to its molecular structure. Because the polymer has the structure that is hydrolytically unstable, it is vulnerable to environmental degradation and became a challenger for the long term survival of polyurethane. [10]

2.1.2 Non-Isocyanate Polyurethane

Due to several drawbacks of conventional polyurethanes, there is substantial interest to develop alternative, environmentally friendly methods for the preparation of polyurethanes (Non-isocyanate routes). In the last few decades, several routes were examined and some examples include (i) reaction of bis(chloroformates) with diamines [11], (ii) adiponitrile carbonate with diols or polyols [12], (iii) reaction of urethane diphenol with phosgene [13], (iv) cyclic carbonates with amines [14], etc. Though these approaches are somewhat more environmentally friendly than conventional method, low degree of polymerization makes these processes less preferable.

Among all methods of non-isocyanate synthesis of polyurethane, reaction of cyclic carbonate with amine is the most attractive. In 1957, Dyer and Scott first reported the use of ethylene carbonate and primary diamines for the preparation of polyurethanes. [15] They discovered that when 2-(hydroxyethyl)-carbamates can be obtained from ethylene carbonate and primary diamines, and subsequently form polyurethanes by losing ethylene glycol when subjected to vacuum distillation with an alcohol at 150 ºC in the presence of catalyst. (Figure 4) However, attempts to synthesize polyurethanes from secondary amines were unsuccessful. They also prepared polyurethanes from amino alcohols such as 1,10-aminodecanol and ethylene carbonate using the same method via the formation of intermediate, 2-(hydroxyethyl)-carbamates.

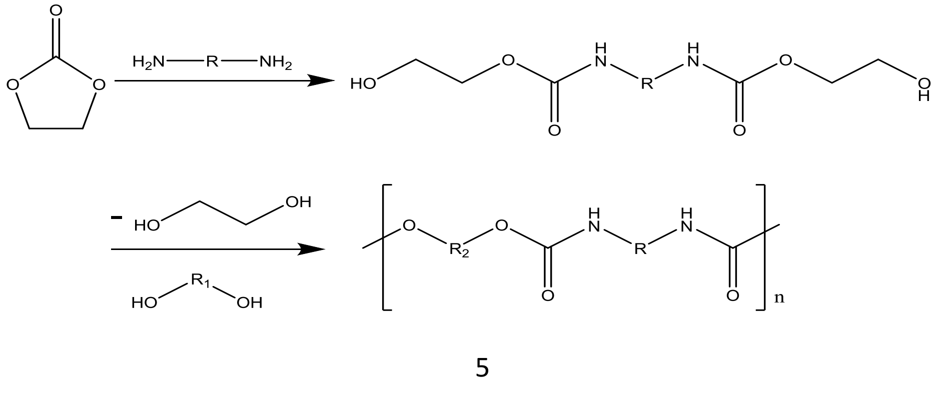


Figure 4 Schematic illustration of synthesis of polyurethane reported by Dyer et al.

The reaction between diamines and cyclic carbonate is known to produce hydroxypolyurethanes, which seems to be most attractive alternative for conventional polyurethane synthesis. [16] Cyclic carbonates, either five or six membered ring, can undergo polymerization reaction with diamines resulting in hydroxypolyurethane. The reaction between cyclic carbonate and diamines can result in two different isomers containing both a urethane and a hydroxyl group, where one isomer has a primary hydroxyl group, whereas the other one has a secondary hydroxyl group. (Figure 5) Due to the formation of hydroxyl group, it can form intermolecular hydrogen bond with the urethane group, which blocks the carbonyl carbon resulting in low sensitivity of the urethane group to hydrolysis; thus hydrolytic stability can be improved. Further, because it is not susceptible to moisture, the application of the coating is not as troublesome as the conventional polyurethane coating. Hydroxypolyurethane usually exhibits increased chemical resistance as well as thermal stability. [17] With increasing awareness of environment, we need to minimize the use of hazardous substances; hence synthesizing polyurethane through the reaction of cyclic carbonates and diamines should be a viable option.

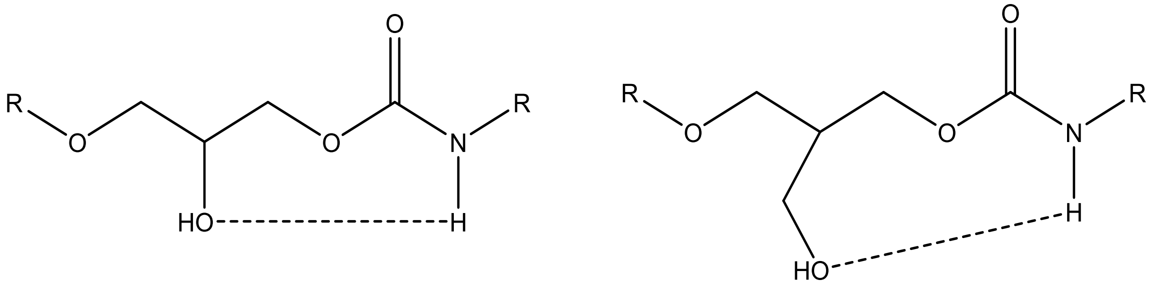


Figure 5 Two different isomers of non-isocyanate polyurethane. PU containing primary alcohol (left) and PU containing secondary alcohol (right)

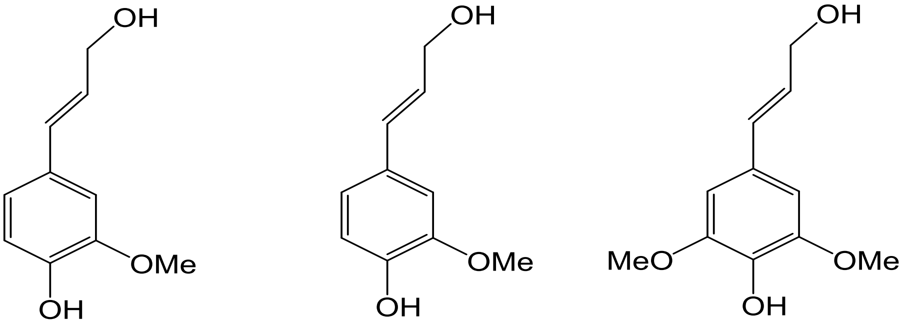
This study proposes to synthesize non-isocyanate polyurethane from 100% sustainable biomass with a green process. The lignin and vegetable oils were be used as the raw materials. The vegetable oils could be converted to epoxidized oils, followed by further conversion to cyclic carbonate using carbon dioxide. Lignin, a complex chemical compound derived from wood and plants and one of the most abundant biomass on Earth, could be converted polyamines. Subsequently, these two modified raw materials will be reacted to produce sustainable polyurethane.

2.2 Lignin

2.2.1 Chemistry of lignin and current application

Lignin is a complex chemical compound most commonly derived from wood, plants, and algae, which is one of the most abundant organic biopolymer available on Earth. It is one of the three major polymeric components found in the cell walls of plant along with cellulose and hemicellulose, which are solely derived from carbon, oxygen, hydrogen and energy from the sun. The role of lignin in plant cell is to act as resin that holds the lignocellulose matrix together, by filling the space between cellulose and hemicellulose, thereby providing the strength and rigidity to the plant stem. [18] Furthermore, lignin helps protecting plants from biological attack and assists water transport to the plant cell walls. The composition, molecular weight, and amount of lignin differ from plant to plant; however, it is estimated that lignin contains 30% of the organic carbon available in plant biomass available. [19]

Lignin is an amorphous, cross-linked, and three dimensional phenolic polymer consisting of methoxylated phenylpropane structures. Typical chemical structure of lignin is shown in Figure 7. [20] Although the exact structure of lignin in nature is still unknown, it is believed that the biosynthesis of lignin involves the polymerization of three primary monomers: *p*-coumaryl alcohol (*p*-hydroxyphenyl), coniferyl alcohol (guaiacyl), and sinapyl alcohol (syringyl), as shown in Figure 6. The common linkages in lignin structure are shown in Figure 8.



p-coumaryl alcohol coniferyl alcohol synapyl alcohol

Figure 6 Major building blocks of lignin

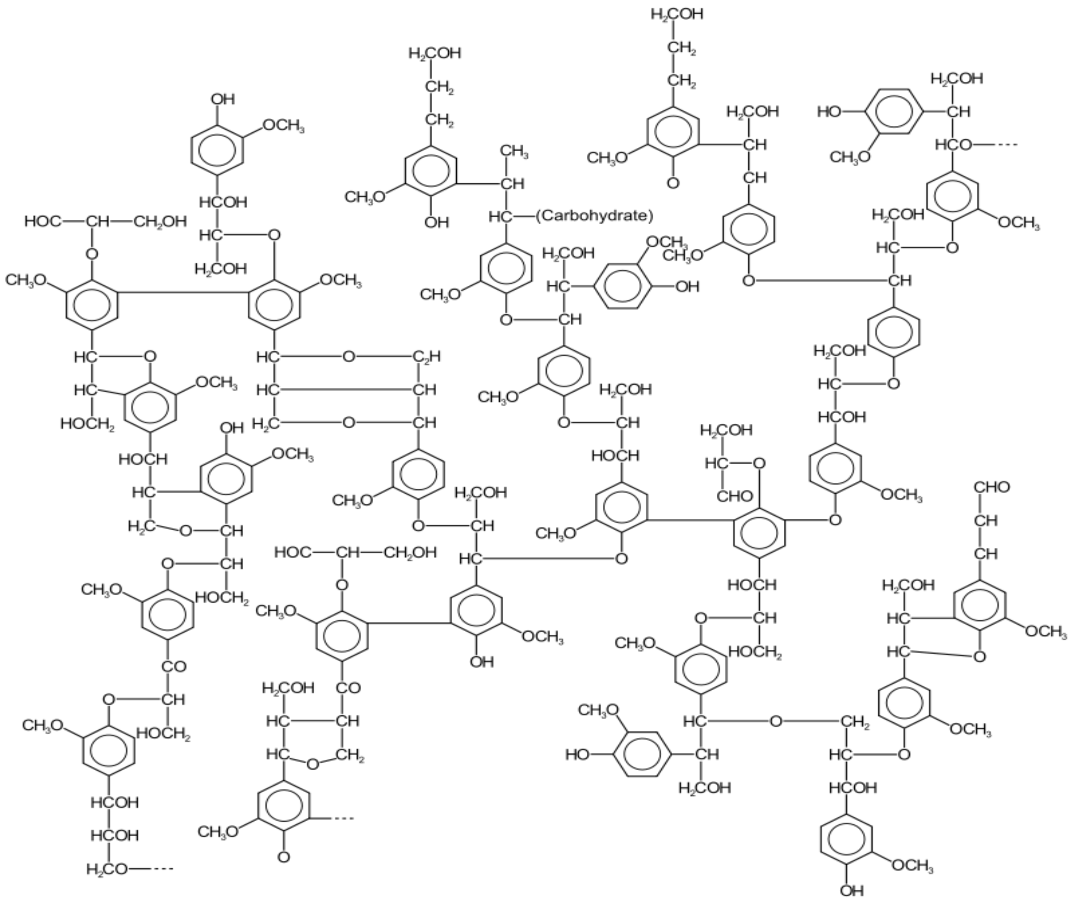


Figure 7 Typical structure of lignin

Currently, commercial chemical pulping processes (Kraft pulping) produce Kraft lignin in the cooking liquor as residue. According to the Food and Agricultural Organization of the United Nations (FAO), in 2006, 9.8×10^7 tons of Kraft pulp were produced in worldwide. [21] The spent cooking liquor from kraft pulp mill, called black liquor which consists of inorganic salts, organic (which lignin makes the majority parts) and water, is sent to the evaporation unit where water is evaporated and the organic material is combusted to generate heat and electricity. The inorganic material left is then recycled to produce new cooking liquor. However, the heat produced by combusting organic material in a modern recovery boiler is more than enough to cover all internal energy use and it creates energy surplus. [22]

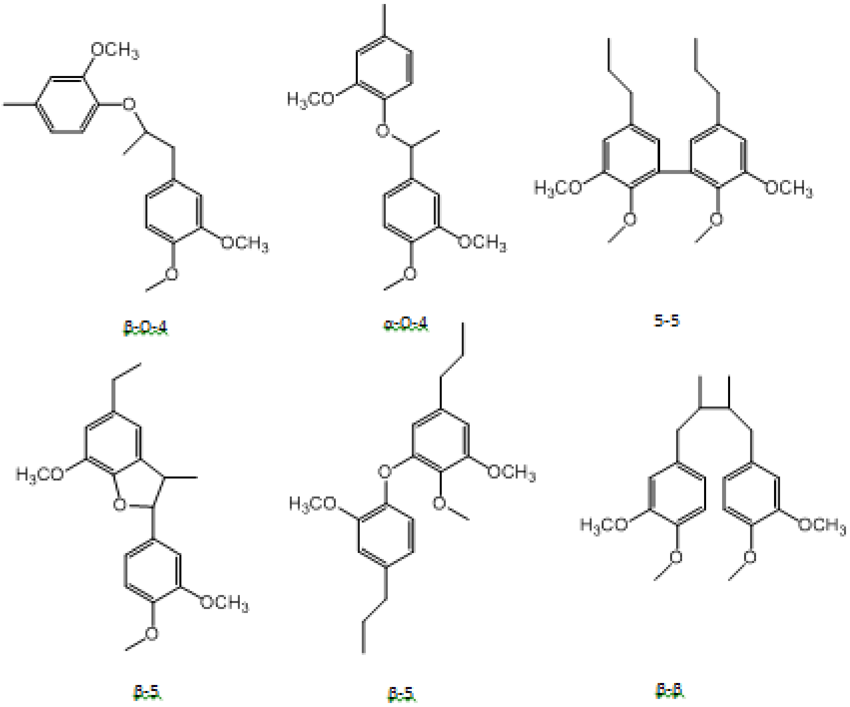


Figure 8 Common linkages found in lignin

As we are in the phase of historic transition, from petroleum based to a biomass-based society, researchers are interested in taking the advantage of the renewable nature of lignin and utilize it to replace petroleum-derived products. In the last few decades, there had been a considerable effort to utilize the large surplus amount of lignin into more useful products. It has been suggested that lignins can be applied as an effectove food stabilization agent due to its antioxidant and antifungal properties. [23] Moreover, anti-carcinogenic and antibiotic activities of lignin have been reported [24]. Also, researchers attempted to substitute petroleum with lignin in several polymers available and these include carbon fiber [25, 26], phenolic resin [27], polyurethane [28] and epoxy-resin [29]. Lignin is also susceptible to a wide range of chemical transformation and can be broken down in to simple monomeric compounds. For example, through catalytic reduction reactions, lignin can break down into simple aromatic compounds such as phenols, benzene, toluene and xylene by removing some of the functional groups of lignin subunits [30]. Subsequently, these small compounds can be used to synthesis other fine chemicals using the technology that is already developed in petroleum industry. However, vanillin and dimethyl sulfoxide are the only two low molecular weight chemicals produced in large quantities [31]. Although there are many applications using lignin, only 1 to 2 % of lignin is used to make other useful chemicals [32]. Therefore, new applications that can consume large amount of excess lignin will be essential in the future.

The promoting factors for utilizing lignin as raw material for polymeric synthesis can be summarized as follows:

- Renewable and abundant source of carbon that takes up approximately 30% of the organic carbon available in plant biomass
- Capability of applying in wide range of chemical reactions due to various reactive points
- Material with intrinsic biodegradability which is expected to transmitted to polymers where lignin is incorporated
- Byproduct of the pulp and biofuel industry that are considered as waste

As it can be seen, lignin is obviously the perfect candidate for the synthesis of sustainable polyurethane and used as one of the raw material for this research.

2.2.2 Lignin-based Polyurethane

Using lignin as one of the raw materials for the polyurethane synthesis has been reported several times before. In 2009, Cateto et al. modified lignin into liquid polyols by oxypropylation process. [33] They prepared polyurethanes with four different types of lignin and the synthesized polyurethanes were comparable with the polyurethane rigid foams prepared with commercial polyols. Moreover, Saito et al. prepared lignin-based polyurethane thermoplastics by reacting with oligomeric polybutadiene diisocyanatye [34]. Robust thermoplastic polyurethanes with high lignin contents (65-70 wt%) was successfully synthesized and discovered that increase in lignin contents enhances the modulus as well as cross linking degree. In addition, Huo et al. prepared polyurethanes by the reaction of a mixture of lignin-amintated polyol and glycol with diphenylmethane diisocyanates in the presence of water as blowing agent [35]. The crosslinking kinetics of the formation of lignin-aminated polyol-based polyurethane foam was studied using FTIR-ATR spectroscopy.

Although several researchers reported lignin containing polyurethane, all of the polyurethane mentioned above involves using toxic isocyanates. Furthermore, other petroleum derived chemicals such as surfactant or polyols had to be incorporated to in order to achieve the mechanical property that is comparable to commercial polyurethanes available. Despite the inclusion of lignin, majority content of polyurethanes are petroleum derived polyols and toxic isocyanate; therefore it cannot be considered as 100% green polyurethane.

2.3 Vegetable Oil

2.3.1 Chemistry of triglyceride

Vegetable oil, which can be derived from plant sources, are found abundance in all parts of the world, which makes it possible for an ideal source of chemical feedstock that can replace petroleum derived chemicals. They are made up of triglyceride molecules, and the general structures are shown in Figure 9. Three fatty acids are connected together by a glycerol with each fatty acid containing 14 to 22 carbons with 0 to 3 double bonds [36]. In last few decades, they have been utilized to replace petroleum chemicals to produce coatings, inks, platsticizers, lubricants, and agrochemicals [37-43].

Since the vegetable oil-based materials are sustainable and biodegradable, the incorporation of vegetable oil not only avoids the use of toxic isocyanate, but also contributes to reducing global warming effects. Moreover, not only natural oleochemicals, such as vegetable oil, has shown great potential to be utilized as a basis for polymers and composites, it also has both economical and environment advantages over petroleum derived chemicals. Hence, vegetable oil is an attractive alternative to be used as one of the raw material for the polyurethane synthesis.

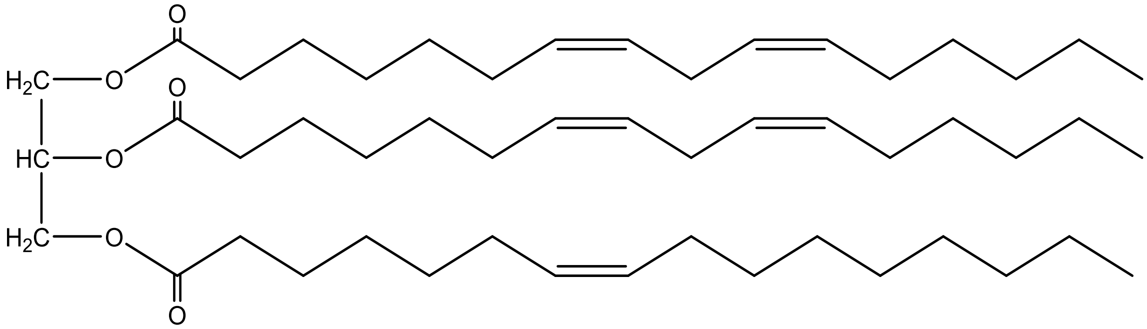


Figure 9 Chemical structure of typical triglyceride

2.3.2 Current application of vegetable oil in polyurethane

Recently, several researchers accomplished to synthesized polyurethane using vegetable oil as material using non-isocyanate reaction route. In 2008, Javni et al. prepared polyurethane by a non-isocyanate route by reacting carbonated soybean oil with diamines [44]. Carbonated soybean oil was reacted with different diamines such as 1,2-ethylenediamine, 1,4-butylenediamin and 1,6-hexylenediamine and cured at 70ºC for 10 hours, and then for 3 hours at 100ºC and polyurethane was formed. The results indicated that when making polyurethanes with vegetable oil with diamines, polyurethane with a wide range of mechanical properties can be produced which will be useful for industrial applications. Furthermore, Suqin Tan et al. prepared rigid polyurethane foam by replacing polypropylene-based polyol with soybean oil-based polyol [45]. As a result, they achieved comparable density, compressive strength and cellular morphology.

Despite the fact that different types of vegetable oil based polyurethane have been prepared, polyurethane from 100% biomass is yet to be reported. For example, in the work from Javni et al. soybean oil based lignin is reported but petroleum derived chemical such as 1,2-ethylenediamine had to be used.

2.4 Non-Isocyanate polyurethane using biomass as raw material

Non-isocyanate polyurethane proposed here is prepared through reaction between cyclic carbonate and polyamines via simple ring opening reaction. The reaction mechanism is shown in Figure 10. The reaction is initiated by the nucleophilic attack of amine into the carbonyl carbon in cyclic carbonate, forming tetrahedral intermediate. In the second stage, deprotonation the tetrahedral intermediate occurs due to the attack of another amine. Finally, the carbon-oxygen is broken, due to the strong electron-withdrawing effect of nitrogen atoms then oxygen ion combines with hydrogen ions to from the polyurethane product. [46] The reaction generally gives two isomers: the polyurethane containing secondary alcohol is formed predominantly, where the isomer with primary alcohol is formed in small quantity.

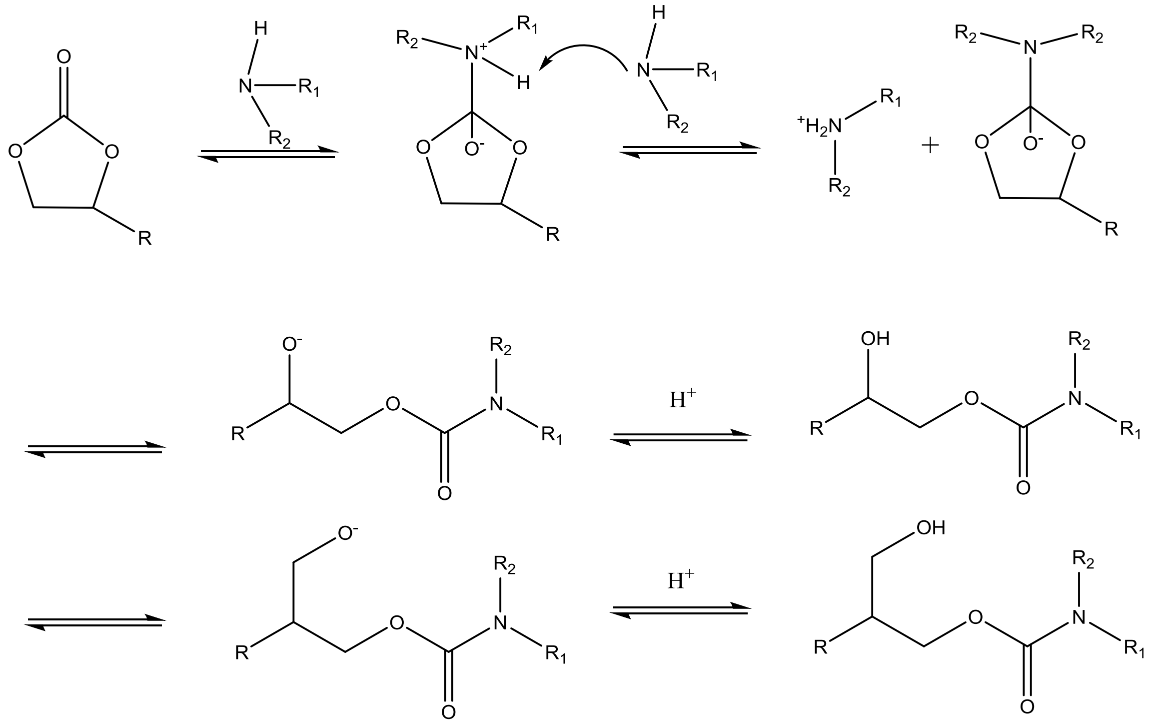


Figure 10 Reaction Mechanism of non-isocyanate polyurethane formation

The reaction is considered to be more effective in high temperatures due to the relatively stable nature of cyclic carbonates [47]. However, excessive high temperature may result in the formation of urea due to the attack of another amine group. Moreover, the aliphatic amines are known to be more reactive towards cyclic carbonates than aromatic polyamines [48]. Also, the reaction rate of cyclic carbonates with amines is also dependent on the initial concentration of the amines [49, 50]. Another factor that accelerates the reaction rate of cyclic carbonate with amine is by activating either monomer by the addition of weak Lewis acid to increase the electrophilicity or the addition of basic additive to amines to increase its nuceleophilicity. It is known that Lewis acids such as lithium chloride is able to activate the cyclic carbonate without deactivating the amine group; therefore the addition of appropriate Lewis acid can result in higher molecular weight of polyurethane [51].

2.5 Modification of biomass as raw materials

2.5.1 Modification of Vegetable Oil into Cyclic Carbonate

Overall, there are two steps for synthesis of cyclocarbonate monomer from vegetable oil. Firstly, the oil will be converted to epoxidized oil, followed by catalytic reaction with carbon dioxide to produce the cyclic carbonate monomer for polyurethane synthesis.

Unsaturated vegetable oil can be epoxidized using hydrogen peroxide in acidic aqueous solution, as shown in Figure 11 [52-53]. The reaction can occur when excessive hydrogen peroxide is introduced to the mixture of the vegetable oil and acidic catalysts aqueous solution with heat. After cooling and neutralizing with water, the separation of oil product from water can be done using 2-methyltetrahydrofuran, which is a green solvent.

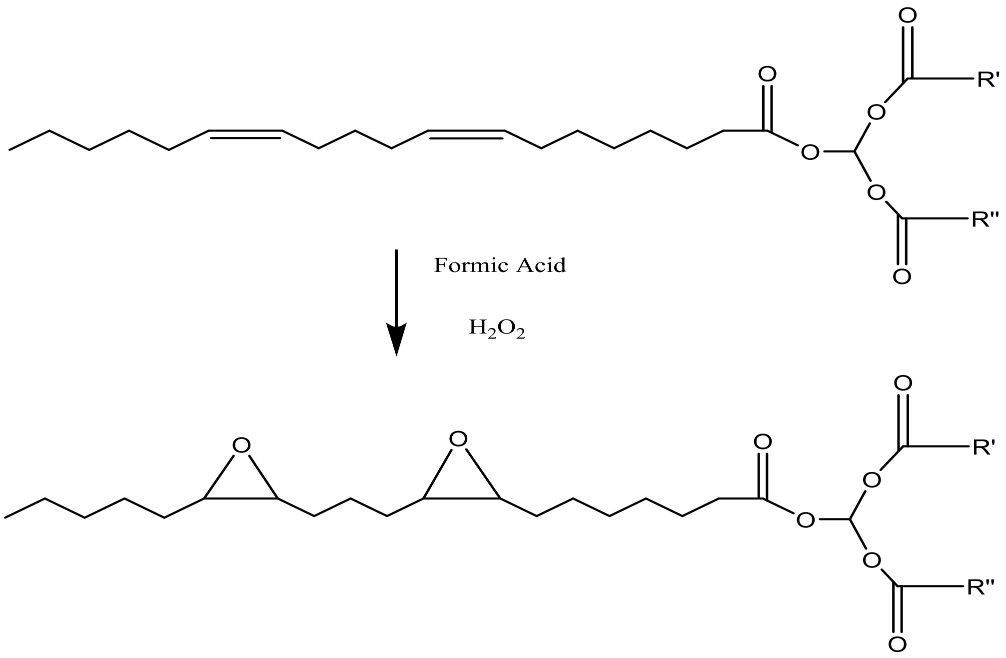


Figure 11 Conversion of vegetable oil into epoxidized vegetable oil

However, epoxidation of various triglycerides has been reported by Swern et al. in 1945 and the reaction was studied and improved until recently to the point where epoxidized triglycerides are available commercially [54, 55]. Out of various epoxidized triglycerides available, epoxidized soybean oil (ESBO) are currently available at a low price and commonly used as a plasticizer in the PVC industry; therefore ESBO was directly purchased from market from the project rather than starting from raw vegetable oil.

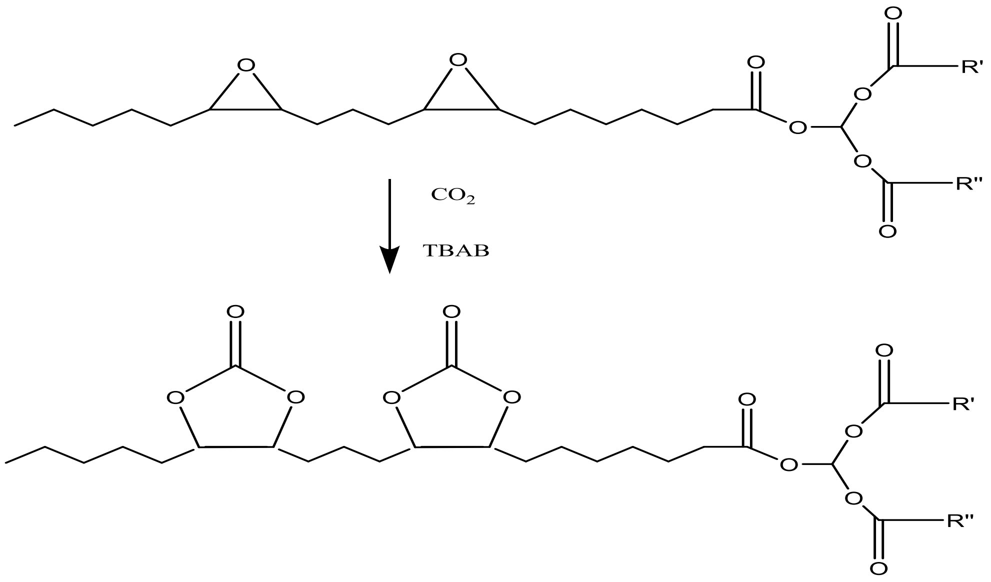


Figure 12 Conversion of epoxidized vegetable oil into carbonate vegetable oil

The epoxidized oil can be further converted into cyclocarbonate, which is the monomer required for NIPU synthesis. The ESBO can be converted to cyclocarbonate by the chemical fixation of carbon dioxide with the presence of catalyst. (Figure 12) The proposed mechanism for the formation of cyclic carbonate monomer is shown in Figure 13. This method involves the ring opening and simultaneous insertion of carbon dioxide into epoxide groups. [56] Typically, the epoxide is activated by the interaction of the oxygen atom with a Lewis acid, followed by the opening of epoxide ring by the nucleophilic attack. Thereafter the opening of the epoxide ring, carbon dioxide as an electrophile attacks the oxygen atom, followed by ring closure, and then the elimination of bromide ion to yield the cyclic carbonate. This is highly efficient method of producing cyclic carbonate monomer and can be conducted at both atmospheric and high pressure.

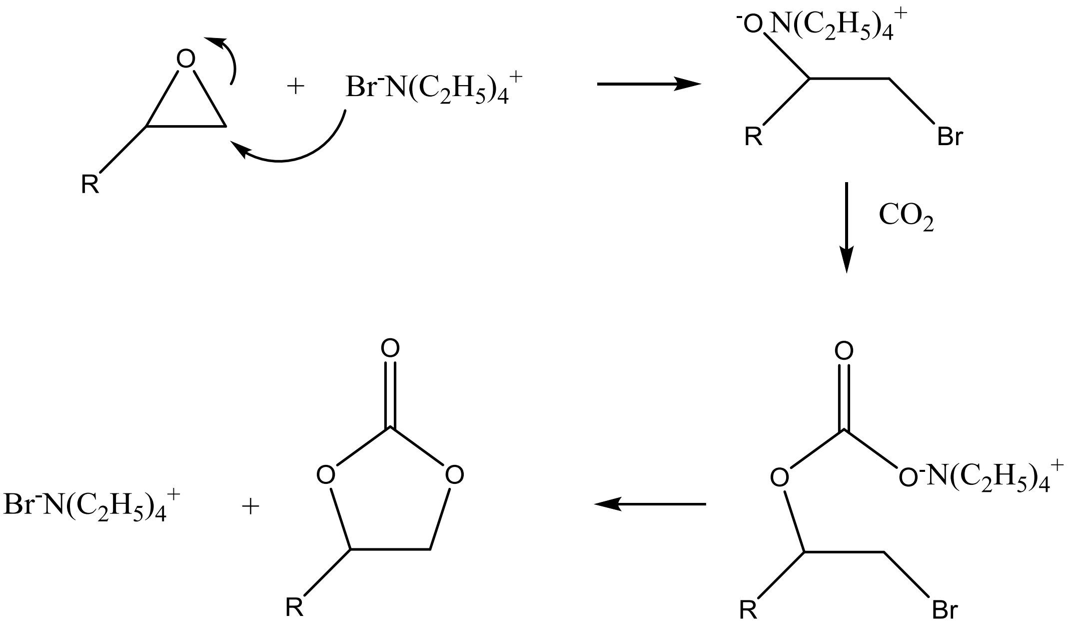


Figure 13 Reaction mechanism of epoxide and carbon dioxide

Transition metal complexes [57], quaternary ammonium halide compound [58], guanidines, amines, quanternary phosphnium compounds [59], etc. have previously been investigated as catalysts. Moreover, alkali metal salt such as potassium bromide (KBr), lithium bromide (LiBr), sodium iodide (NaI), etc have been studied, but resulted in low to medium conversion [60]. Among all the catalysts have been studied, quaternary ammonium halide, especially tetrabutylammonium bromide (TBAB) is most commonly used and known to be effective. TBAB at 5% molar concentration with respect to epoxy group has shown to give maximum conversion of epoxy group into carbonate groups. [61] It is also known that the catalytic activity of quaternary ammonium salts increases when the nucleophilicity of halide anion such as bromide and Lewis acidity of the cation, which is tetrabutylammonium in this case, increases. In addition, the TBAB system has an advantage in that the catalyst can be easily removed from the product by thermal breakdown of molecule into volatile products by the Hofmann elimination reaction.

(Figure 14) [61] The temperature where the breakdown of catalyst occurs is well below the breakdown temperature of vegetable oil. It is known that the thermal decomposition of vegetable oil occurs between 288-306 ºC [62] and the thermal decomposition of the catalyst begins around in 150-190 ºC.

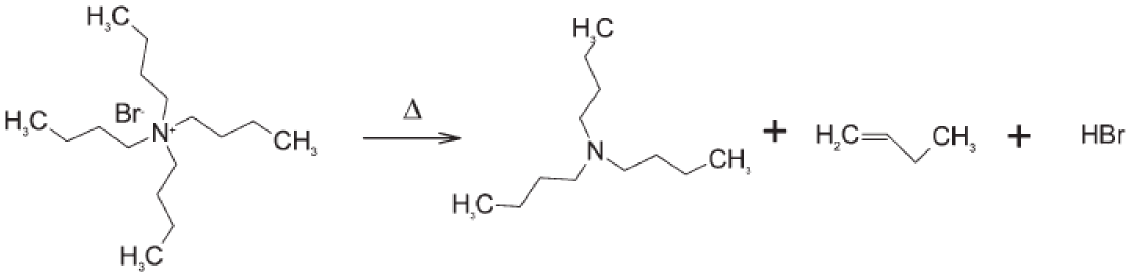


Figure 14 Thermal decomposition of TBAB through Hofmann elimination

Furthermore, this process has two great major advantages respect to the environment. Firstly, this process occurs in solventless system because the vegetable oil itself can act as solvent which dissolves both the catalyst and carbon dioxide; hence it is eco-friendly. Secondly, this process utilizes carbon dioxide as a sustainable reactant; it is the cheapest and the most abundant source of carbon available which is also non-flammable and has low toxicity.

2.5.2 Modification of lignin and preparation of polyurethane

While soybean oil can be converted into cyclic carbonate, the other natural raw material lignin can be converted into polyamines. Researchers have reported few ways of converting phenolic compounds into amino-phenolic compounds such as the nitration of phenol [63], and further reduction into amine group using appropriate catalyst [64]. Another approach also reported is direct conversion of phenol into aniline via Smiles rearrangement [65]. For this research, coupling lignin with organosilane due to the organosilanes' capability of being easily grafted with polar –OH groups present in lignin. Further description about the approach and mechanism will be explained in later section.

2.5.2.1Oragnosilane

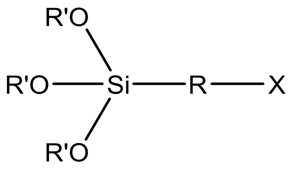


Figure 15 Checmial structure of typical organosilane

Monomeric silicon chemicals are known as silanes and any chemical that contains at least one carbon-silicon bond is known as an organosilane. Generally, organosilanes contain three key elements beside silicon atom and the structure is shown in Figure 15. X represents for an organic moiety that is non-hydrolysable which can be either reactive or non-reactive depending on its type. OR' is a hydrolysable group such as alkoxy or an acetoxy is known to be unstable when present with hydroxyl groups. Finally, R is a space moiety, which can be aryl or alkyl chain.

Typically, due to the dual reactivity of organosilane, both alkoxy group (OR') and non-hydrolysable organic moiety (X), it is used to couple inorganic or organic substrates such as minerals, metals or cellulose and polymeric matrices such as rubber, thermoplastic or thermosets to improve its physical properties. The applications include adhesion promoter, dispersing/hydrophobing agent and crosslinking agent [66].

The known mechanism of the interaction of organosilane with –OH group of organic polymer is composed of 4 steps: (a) Hydrolysis, (b) Self-condensation, (c) Adsorption and (d) Chemically grafting [67].

a. Hydrolysis: When the organosilane monomers are introduced into water with a catalyst which can be either acid or base, the –OR' group undergoes hydrolysis which produces alcohol and yield reactive silanol group (–Si-OH).

    I. Acid catalyzed hydrolysis: During the acid catalyzed hydrolysis, the leaving OR’ group is protonated by the acid and is displaced by the attack of water.
    II. Base catalyzed hydrolysis: It involves the attack of hydroxyl ion to displace alkoxy group into hydroxyl.

b. Self-condensation: While the silane goes through hydrolysis process, the self-condensation of between the free silanol groups, forming –Si-O-Si- linkages. In most cases, this step is not favored and should be minimized in order to leave the silanol groups free to graft with –OH groups on the organic polymer matrices. The condensation reaction rate can be controlled by adjusting the pH of the environment and it is reported that an acidic pH setting usually accelerates the hydrolysis reaction but slows down the self-condensation reaction. [68]
c. Adsorption: The reactive free silanol is adsorbed and forms hydrogen bond with hydroxyl groups of the organic polymer. During this process, free silanols can react with each other to form polysiloxane structures linked with –Si-O-Si- bond.
d. Chemically grafting: Finally, the hydrogen bond between silanol and hydroxyl group can be converted into the permanent covalent –Si-O-C- bond by heating and liberating water. During this process, the free silanols will also condense each other.

The figure describing the mechanism of organosilane on the hydroxyl group of polymer matrices is shown in Figure 16.

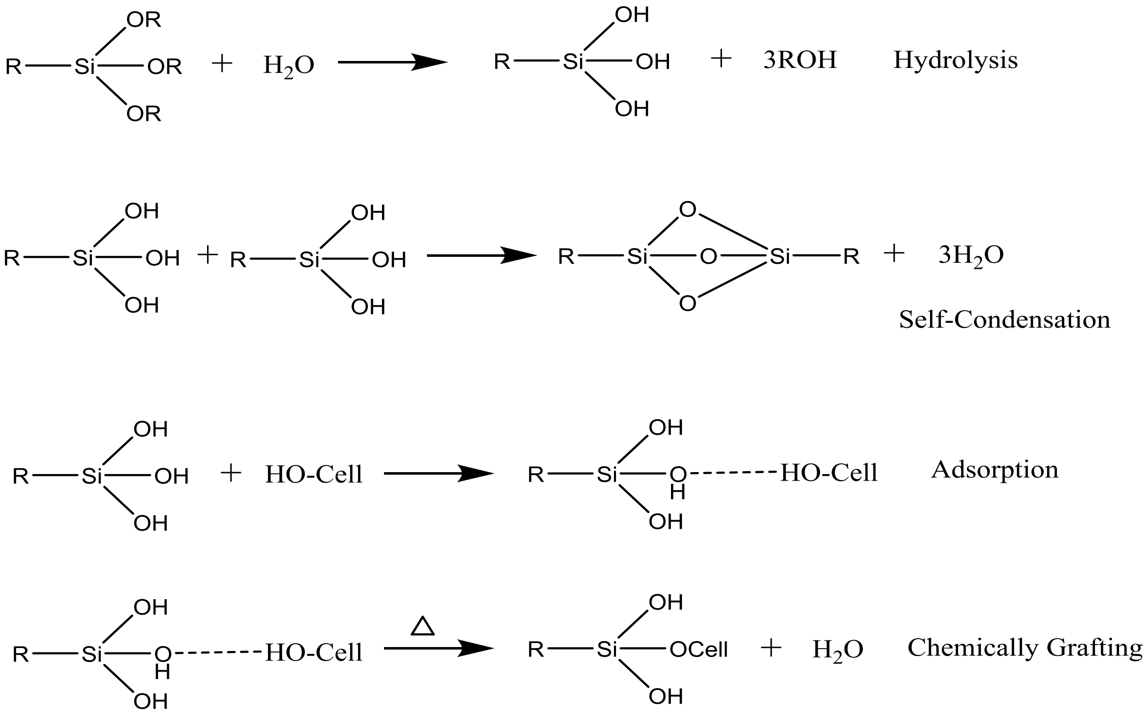


Figure 16 Reaction mechanism of organosilane and hydroxyl group

2.6 Preparation of green polyurethane

Although the coupling reaction of organosilane is generally applied to the surface of organic polymer to enhance its performance, it can also be applied to the modification of lignin since lignin has free –OH group. For this project, 3-aminopropyltriethoxysilane (APES) was chosen as the coupling agent to modify the lignin which has the amine functional group as the organic moiety. APES was chosen for two main reasons: it possess amine functional group which is readily reactive with cyclic carbonate to form urethane bond, and reactive alkoxy group of APES can easily grafted to Ph-OH group of lignin through one pot reaction. The structure of APES is shown in Figure 17. In 2004, M. Castellano et al. investigated that phenolic –OH group attached to lignin is more reactive towards silane chemicals due to its more acidic characteristic than aliphatic –OH groups of other polymers such as cellulose [69]. Therefore more electrophilic nature of Ph-OH gives rise to condensation with silanol groups. The reaction scheme is shown in Figure 18.

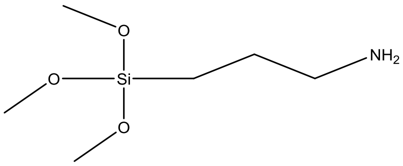


Figure 17 Chemical structure of 3-aminopropyltriethoxysilane

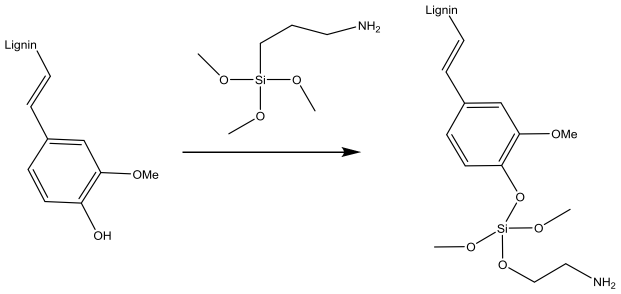


Figure 18 Schematic illustration of reaction of lignin and APES

The ideal result would be to attach one molecule of APES per one Ph-OH functional group. However, there is always the side reaction, which is the self-condensation between silane molecules. Inappropriate control of the reaction condition such as time, temperature and pH would cause the formation of complex 3-dimensional molecule as a result of the condensation of the coupling agent. (Figure 19) [70]. Especially for the synthesis of polyurethane, this is troublesome for two main reasons. Firstly, the formation of complex three dimensional molecules gives poor solubility in the most of organic solvent which is not favored for the further use of the modified lignin i.e., the synthesis of polyurethane. Secondly, due to the formation of three dimensional structures, exact analysis of the amination degree can be challenging. When preparing non-isocyanate polyurethane, the initial amine concentration is very important because it can easily change the physical properties of the final product; however if the amine concentration of the modified lignin cannot be analyzed precisely, it will be problematic in preparing polyurethanes with the property desired.

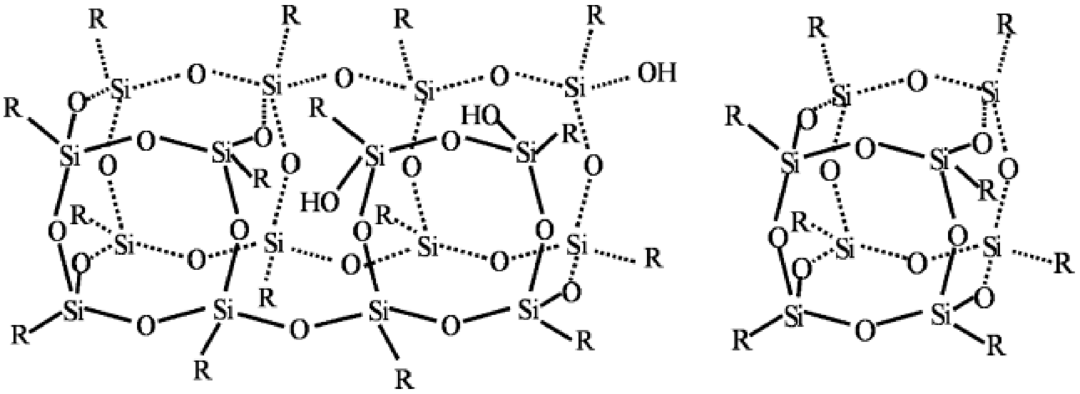


Figure 19 Example of complex three dimensional molecule from after self-condensation reaction of organosilane molecules

Therefore, to resolve the two problems mentioned above, the reaction step had to be altered. Instead of modifying the lignin first, urethane monomer was synthesized. As shown in Figure 20, APES and carbonated soybean oil (CSBO) was reacted in a dry media with the presence of catalyst, lithium chloride. As the reaction processes in dry condition, alkoxy group of APES becomes stable and the self-condensation can be prevented. After the complete conversion of the carbonate groups into the urethane linkages, lignin is introduced into the urethane monomer with water for the polymerization as depicted in Figure 21. The advantage of this reaction is that this can be done in one pot reaction with relatively easy process.

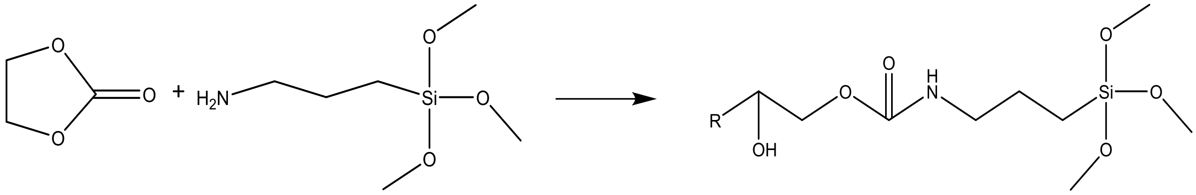


Figure 20 Schematic illustration of reaction between APES and cyclic carbonate

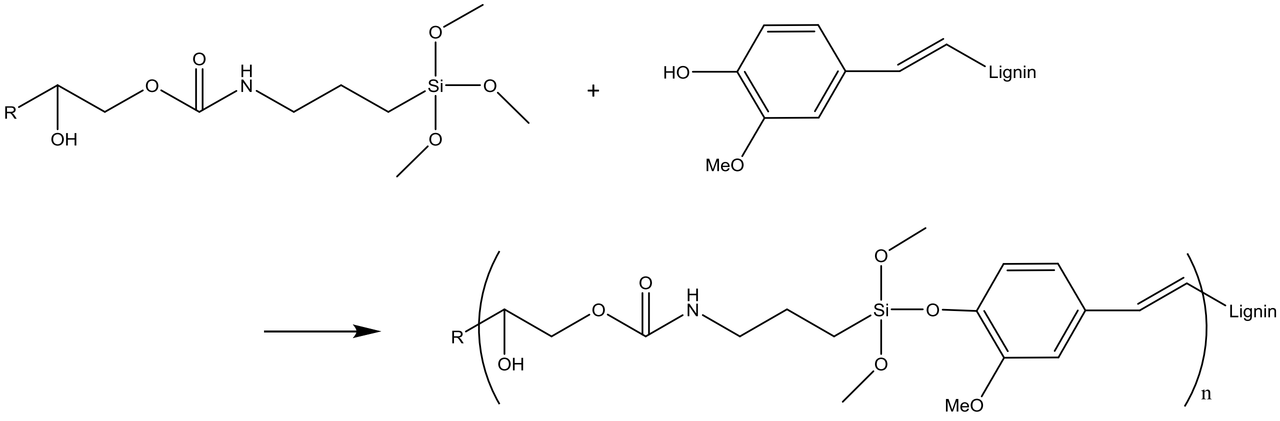


Figure 21 Schematic illustration of polymerization reaction between lignin and urethane monomer to form polyurethane

2.7 Summary of proposed synthesis route

The studied route for the synthesis of polyurethane can be summarized as following:

1) Modification of epoxidized soybean oil to synthesized urethane monomer through the chemical fixation of carbon dioxide (Figure 22)

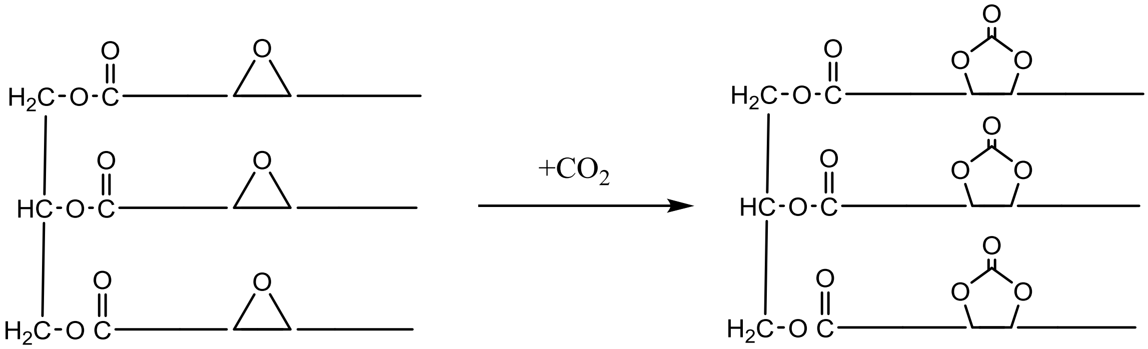


Figure 22 Formation of carbonated soybean oil

2) Synthesis of urethane monomer through the reaction between CSBO and APES (Figure 23)

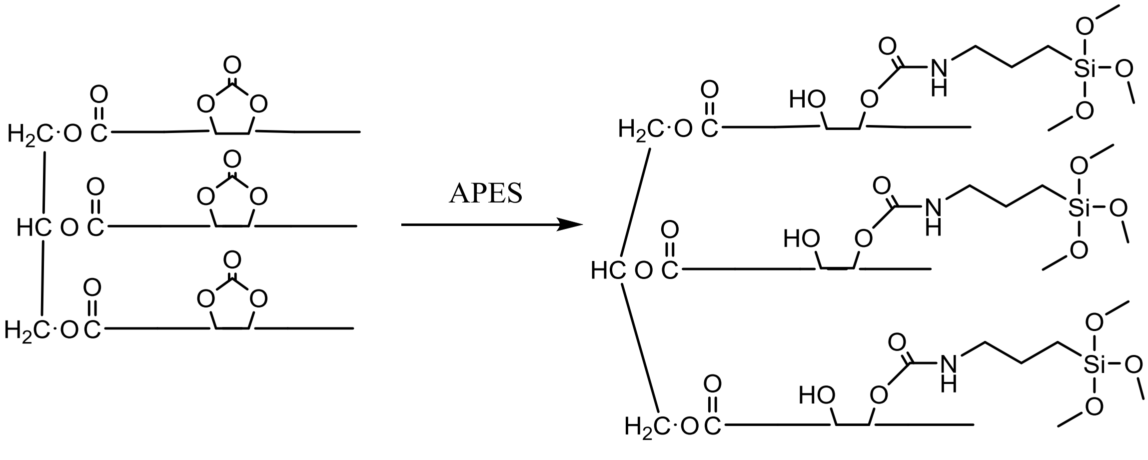


Figure 23 Synthesis of urethane monomers

3) Synthesis of sustainable lignin/soybean oil-based polyurethane (Figure 24)

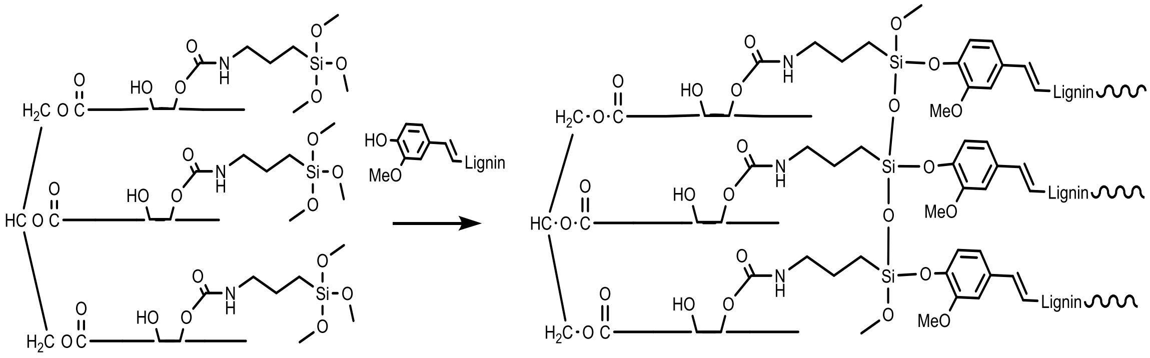


Figure 24 Schematic illustration of synthesis of sustainable polyurethane

Carbonated soybean oil, which is step 1, will be synthesized separately, and remove the catalyst, while step 2 and 3 will be done in one pot reaction. In this polymer, aromatic structure of lignin will function as hard (rigid) segment, while polysiloaxne, -Si-O-Si- linkages formed as a result of self-condensation of APES molecules will function as soft segment

3. Materials and Methods

3.1 Materials

Epoxidized soybean oil (Spectrum Chemicals, CAS 8013-07-8), Tetra-n-butylammonium bromide (TBAB) (VWR, 99+%, CAS 1643-19-2), carbon dioxide (AirGas 50 lb industrial grade, CGA 320) , Kraft Lignin (Sigma-Aldrich, CAS 8068-05-1), tetrahydrofuran (Sigma-Aldrich, 109-99-9), 3-aminopropyltriethoxysilane (Sigma-Aldrich, >98%, CAS 919-30-2), lithium chloride (Sigma-Aldrich, anhydrous, >99%, CAS 7447-41-8), ninhydrin (Sigma-Aldrich, CAS 485-47-2), dimethyl sulfoxide (BDH Chemicals, CAS 67-68-5) and dimethyl sulfoxide (Sigma-Aldrich, 99.96 atom %D CAS 2206-27-1) were used as received

3.2 Methods

3.2.1 Preparation of carbonated soybean oil (CSBO) and characterization

100 g of ESBO was placed in a 500-mL three neck round bottom flask and heated in an oil bath to 140 ºC. Then, 6.6 grams of TBAB (6.6 weight percent or 5 mole % with respect to the epoxy content) was added and continuous flow of carbon dioxide was introduced at a rate of 0.2 mL/s. The reactor was mechanically stirred at the speed of 500 rpm for 72 hours and was operated at the atmospheric pressure.

3.2.2 Preparation of amino lignin and characterization

Reaction between APES with lignin was experimented in order to confirm the capability of lignin being coupled with organosilane. The typical procedure is the following: kraft lignin was dissolved in tetrahydrofuran/water 60/40 v/v, and then the mixture was heated at 50 ^{0}C and stirred for 30 minutes. Then 3-aminopropyltrimethoxysilane (13822-56-5, Sigma Aldrich) was added in large excess with respect to the –OH groups present in lignin, typically at 100:1 ratio. After four hours of stirring at 50 ^{0}C, the solvent was removed at reduced pressure and washed with water and acetone to remove any unreacted APES, and then vacuum dried for 12 hours.

3.2.3 Preparation of Urethane Monomer

In a round bottom flask, 3 grams of CSBO and 5 mol % of lithium chloride respect to cyclic carbonate group was dissolved in 20 mL of THF. Then, 3-aminopropyltriethoxysilane (molar ratio of CSBO: APES was 1:1) was dropped in to the reaction system. The mixture was heated up to and kept at 70ºC for 3 hours under stirring. The reaction progress was monitored by FTIR spectroscopy

3.2.4 Preparation of lignin-soybean oil polyurethane

After 3 hours of reaction of the preparation of urethane monomer, the solution of lignin dissolved in tetrahydrofuran/water 60/40 v/v was added. The reaction mixture was stirred for 12 hours, then was poured into mold and air dried for 2 hours followed by curing at 60ºCfor 7 hours. Various lignin contents were studied.

3.3 Characterization

3.3.1 Fourier Transform Infrared Spectroscopy

FTIR spectroscopy was performed on Nicolet 6700 FTIR spectrometer with a potassium bromide (KBr) beam splitter. A total of 32 scans were taken with a resolution of 4 cm^{-1}.

3.3.2 Nuclear Magnetic Resonance

Samples were prepared by dissolving approximately 25 mg of sample in 500µL of $CDCL_3$ and DMSO-d6. The sample was then analyzed by using Bruker Avance III-400 solution NMR spectrometer with 32 scans at 293 K.

3.3.3 Ninhydrin Test

Ninhydrin is a chemical used to detect primary and secondary amines. It is a visual measurement of existence of primary and secondary amine groups in a system by changing color to a blue to blue-violet color. 4 mg of ninhydrin (1,2,3-indanetrione monohydrate) was dissolved in 1 mL of dimethyl sulfoxide, and about 2 mg of sample was added. The solution was heated and boiled for about 20 seconds, and the final color of the solution was observed and recorded.

3.3.4 Tensile Testing

Mechanical properties were tested on Instron universal materials testing machine equipped with a 10kN load cell with grip length 5cm and rate of grip 5mm/min

4. Results

4.1 Synthesis of carbonated soybean oil (CSBO)

The conversion of ESBO into CSBO was first monitored by FTIR spectroscopy as shown in Figure 22. By comparing the spectrum of ESBO and CSBO, following characteristics should be addressed: two peaks at 833cm^{-1} that represents epoxy absorption has disappeared, while new peak at 1,802 cm^{-1} has appeared due to the formation of the cyclic carbonate moieties. Since FTIR provides qualitative results rather than quantitative results, 100% conversion of ESBO into CSBO was confirmed via ^{1}H-NMR spectrum. It is clear from Figure 26 that the original epoxy groups at δ = 2.80 – 3.20 has disappeared while the new signals at δ = 4.45-5.10 corresponding to the cyclic carbonate group has appeared.

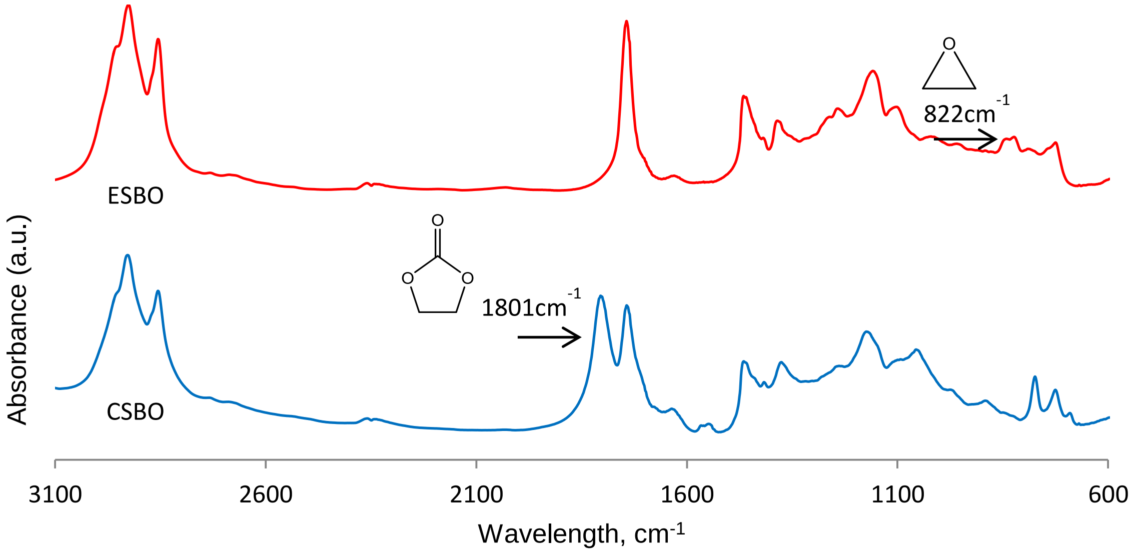


Figure 25 FTIR spectrum of ESBO (top) and CSBO (bottom)

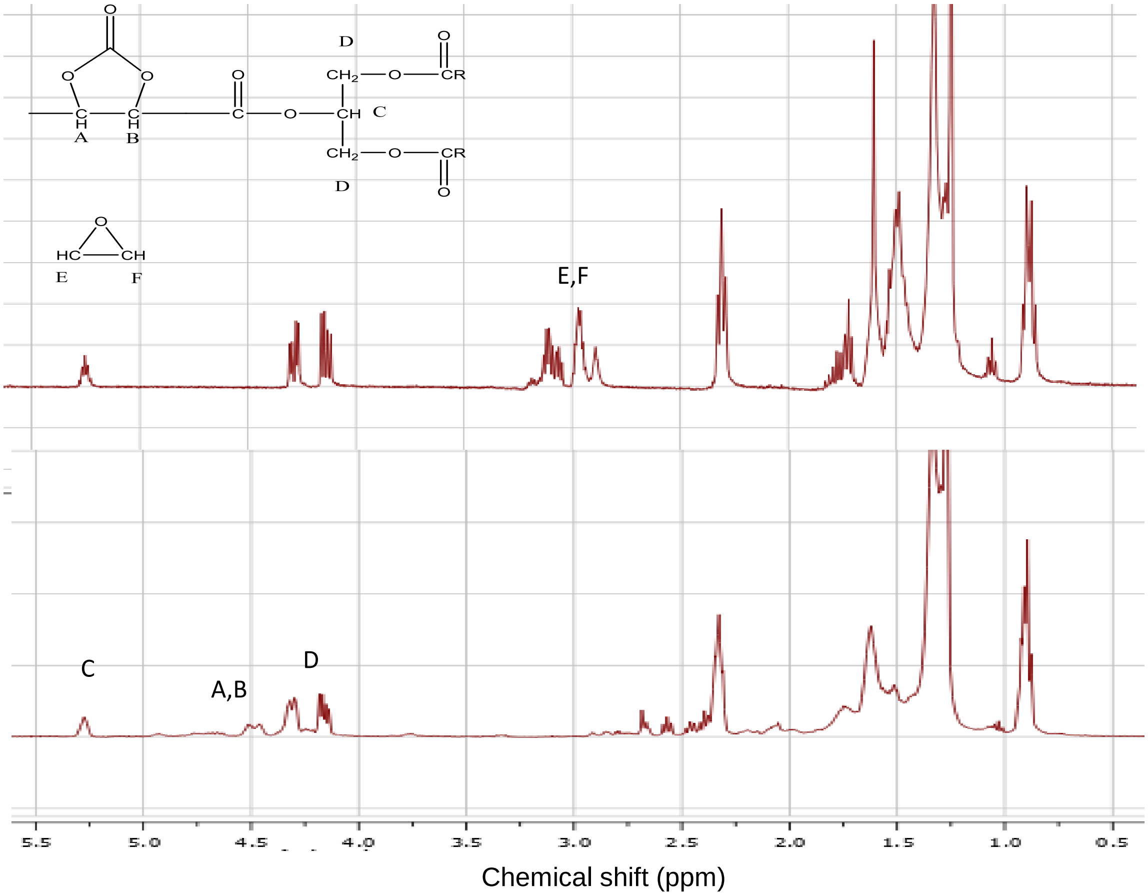


Figure 26 NMR Spectrum of ESBO (top) and CSBO (bottom)

4.2 Synthesis of amino-lignin with 3-aminopropyltriethoxysilane

After the separation and the purification of amino-lignin synthesized, the product was first tested with ninhydrin to determine qualitatively whether it has amine function group present or not. . According to Figure 27, original lignin failed to change color, but changing of color of aminated lignin samples visually proved the introduction of the amine groups.

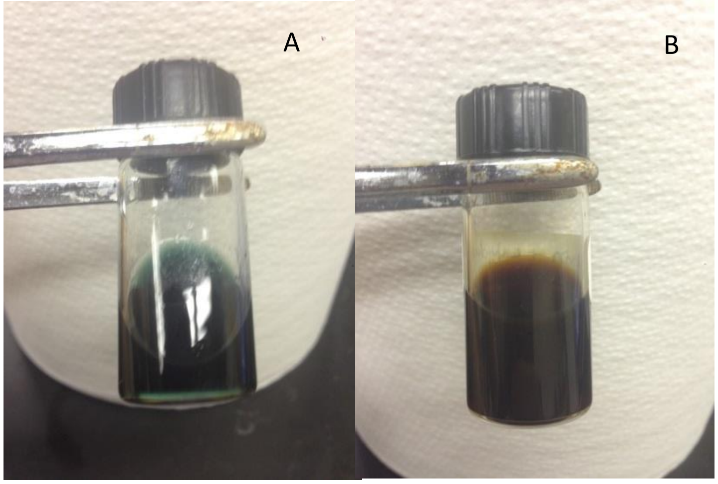


Figure 27 Color reactions of aminated lignin (a) and original lignin (b)

The covalent bonding between APES and lignin was analyzed with FTIR and NMR spectroscopy. Figure 28 shows the FTIR spectrum of modified (top) and unmodified (bottom) lignin. Characteristic peak at 1635 cm^{-1} occurs at modified lignin due to –NH_2. Moreover, in the spectrum of modified lignin, asymmetric Si-O-Si stretching at 1130cm^{-1} and 1031cm^{-1} can be observed. These two peaks can show that 3-aminopropyltrimethoxysilane has been grafted to lignin successfully.

In addition, Figure 29 displays ^{1}H-NMR spectrum of modified and unmodified lignin. The formation of covalent bonds between lignin and APES is associated with disappearance of broad signal between δ=8.00 – 9.00 ppm due to phenolic hydroxyl groups. Also, the appearance of amine proton around δ=1.5 ppm can also demonstrated the coupling of lignin and APES. Therefore, from three different characterization tests, it is confirmed that lignin can be successfully grafted with APES and can polymerize with urethane monomers synthesized.

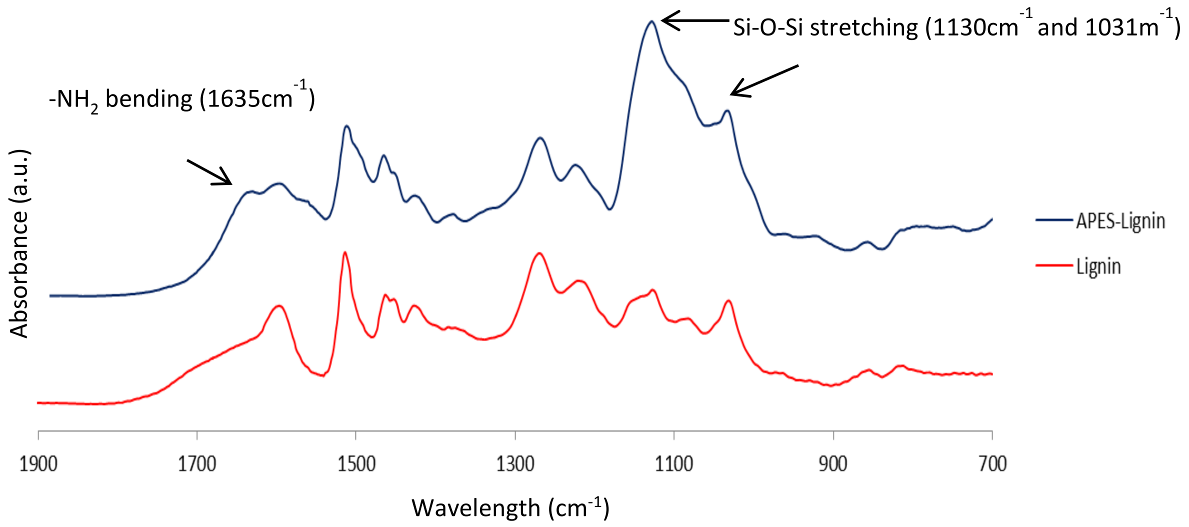


Figure 28 FTIR spectra of lignin coupled with APES (top) and original lignin (bottom)

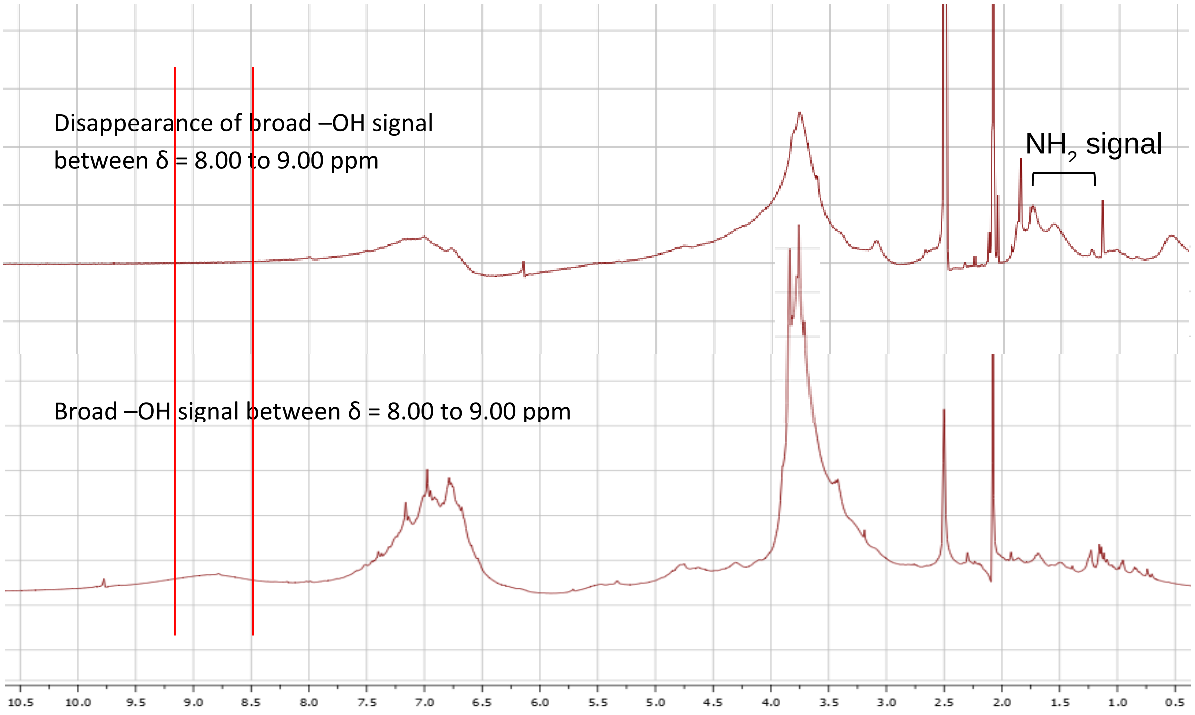


Figure 29 ^{1}H-NMR spectra of lignin coupled with APES (top) and original lignin (bottom)

4.3 Synthesis of urethane monomer

The kinetic behavior of APES and CSBO was investigated to optimize the reaction time before the synthesis of polyurethane. Reacting too long before the addition of lignin can possibly cause polymerization of urethane monomers itself, whereas reacting for insufficient time can remain the majority of cyclic carbonate group unreacted, resulting in not enough urethane linkage formation.

Initially, the reaction was carried without the catalyst, LiCl at 70 ºC and the reaction was monitored with FTIR. As shown in Figure 30, even after 24 hours of reaction, the absorption band of cyclic carbonate group is still observed at 1800cm^{-1} though it shows the formation of urethane linkage at 1730 cm^{-1}. The reaction finally went to completion after 40 hours. On the other hand, when APES and CSBO was reacted with the presence of the catalyst LiCl, the reaction went to completion in just 3 hours. Therefore, the reaction time of 3 hours was chosen for the urethane monomer formation for the synthesis of sustainable polyurethane in the future. In addition, the characteristic peak corresponds to Si-O-C of APES at 1078 cm^{-1} appears after the reaction [71], which shows that the ethoxy group of APES is not hydrolyzed; therefore the urethane monomer has been successfully prepared and 3 hours was chosen as the reaction time for the synthesis of urethane monomer.

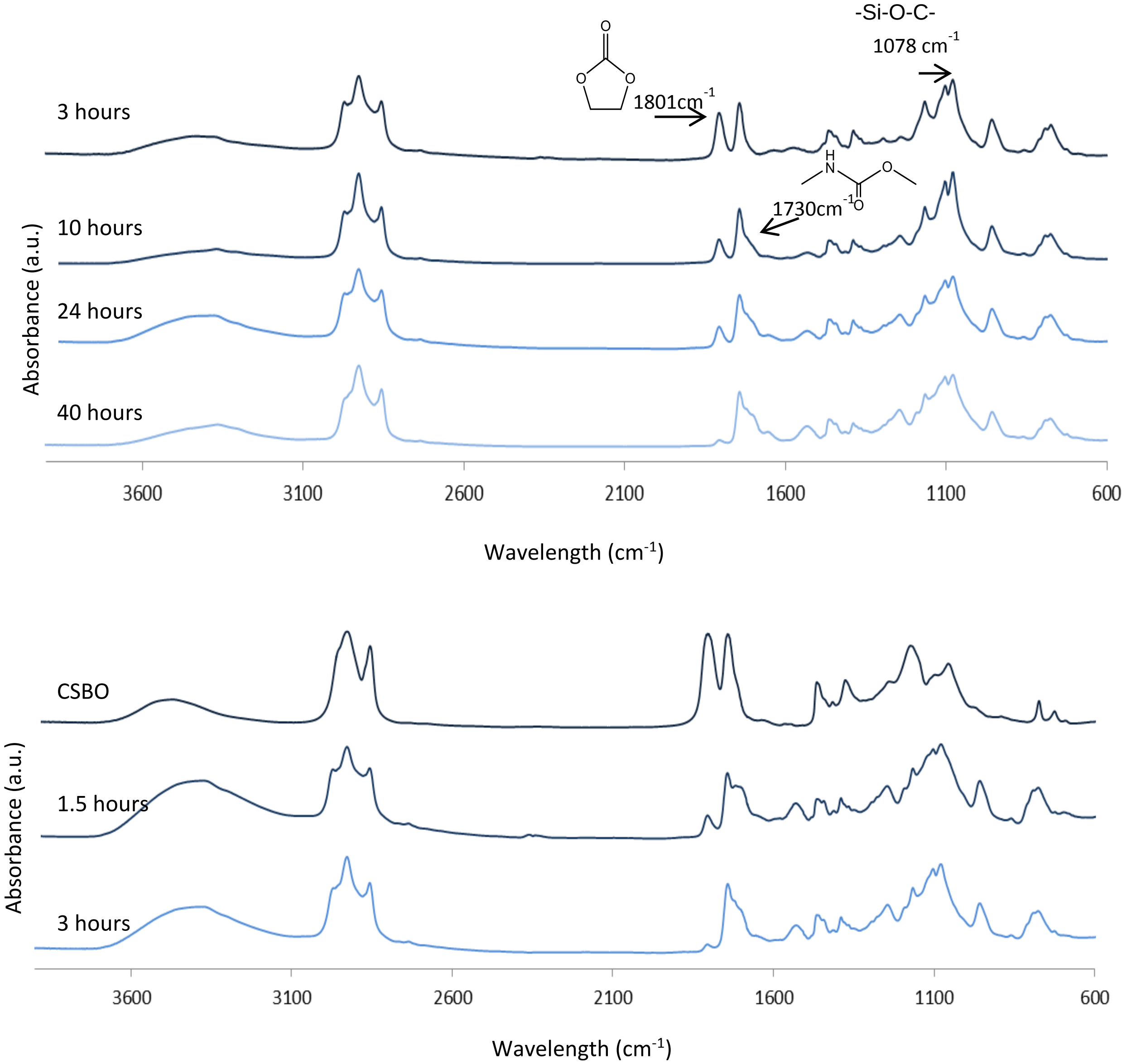


Figure 30 Reaction progresses of CSBO and APES over time without catalyst (top) and with catalyst LiCl (bottom)

4.4 Synthesis of sustainable polyurethane

A series of polyurethane with various lignin contents were successfully synthesized. The picture of thermoplastic lignin polyurethane is shown in Figure 31. In Figure 32, the peak at 1801 cm^{-1} corresponding to the cyclic carbonate group of CSBO disappears and as a result, new peak at 1710 cm^{-1} appears which represents the urethane linkage (-NHCOO-). Moreover, Si-O-Si vibration occurs at 1043 cm^{-1}, but it overlaps with the peaks of CSBO [72]. The appearance of Si-O-Si is due to the self-condensation of APES, which is inevitable phenomenon occurs during the polymerization process. Moreover, the formation of covalent linkage between the aromatic lignin and APES can be explained by the position shift of aromatic bands around 1600 cm^{-1} [73]. As shown in Figure 33, the position shifts of the lignin aromatic bands (1,2) to (3,4) gives clear evidence of the covalent bond formation between phenolic –OH of lignin and APES.

Figure 31 Photos of polyurethane sample synthesized

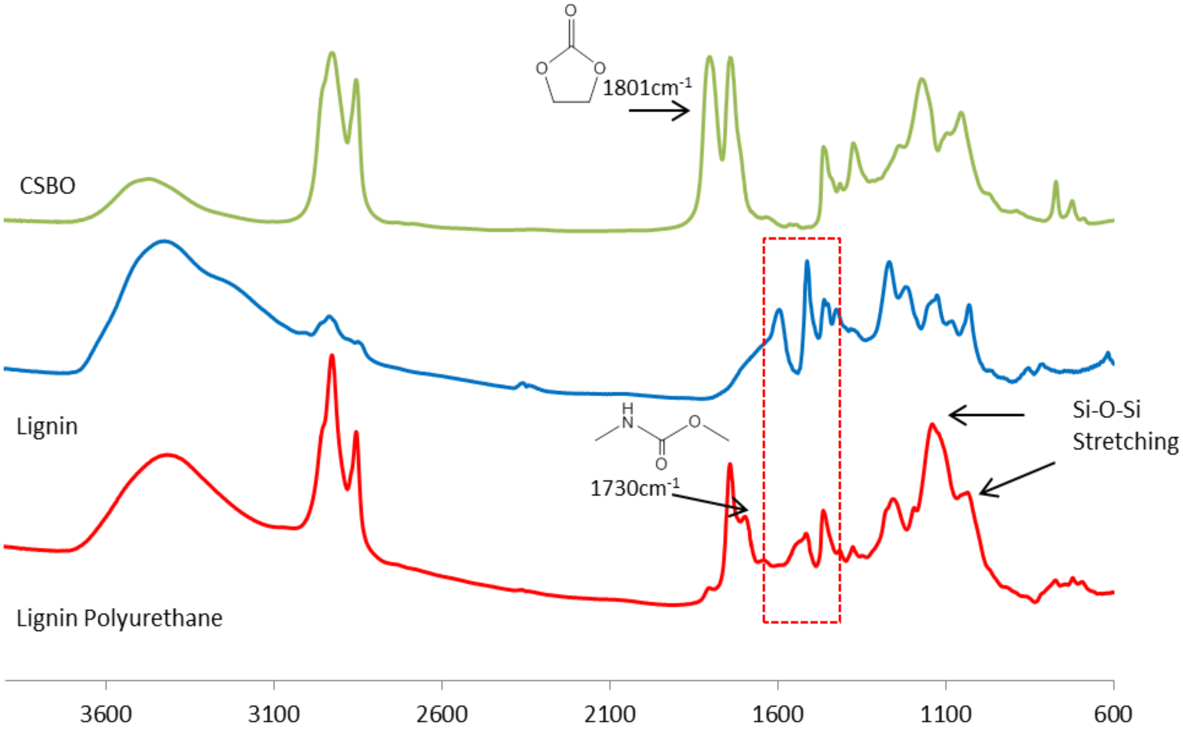


Figure 32 FTIR spectra of lignin polyurethane, lignin, and carbonated soybean oil

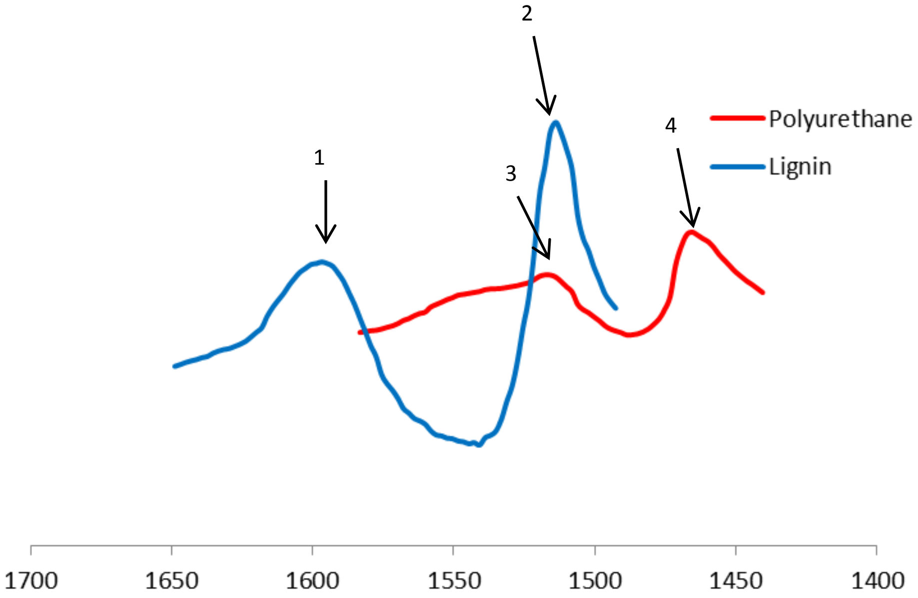


Figure 33 FTIR spectrum of polyurethane and lignin at 1650-1450 cm^{-1} region

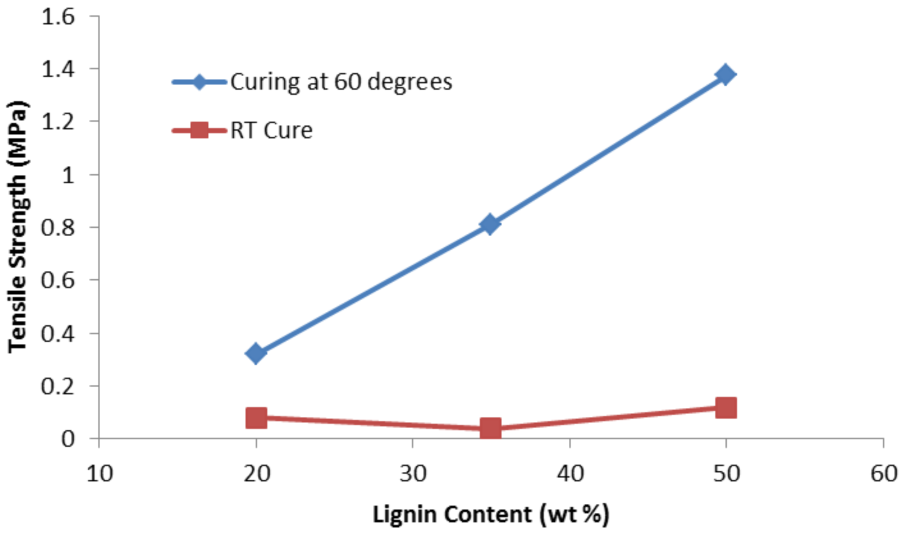


Figure 34 Tensile strength of lignin polyurethanes with different lignin contents

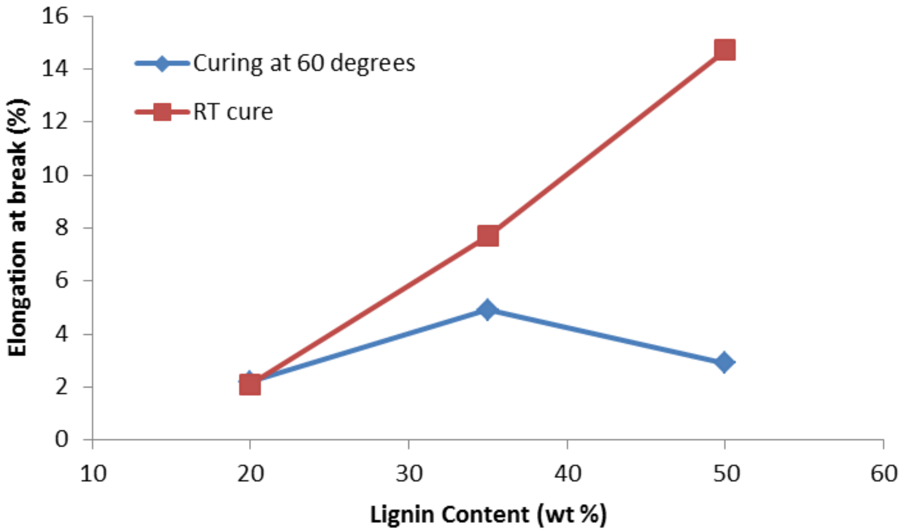


Figure 35 Elongation at break of lignin with different lignin contents

The polymer was prepared through two different casting methods: one is by drying at room temperature, while the other one is by curing at 60 ºC. The tensile strength and the elongation at break of the lignin polyurethane are shown in Figure 34 and 35. As it can be seen, dramatic increase of tensile strength can be observed when it was cured at high temperature. This is obvious because due to the rigidity of lignin aromatic structure and lignin acting as a crosslinking agent, which lead to the formation of three dimensional structure of polymer as a result of curing at higher temperature. This behavior is in good agreement with literature result on the effect of lignin on tensile strength of polyurethane [74]. Moreover, the increased degree of crosslinking will increase with the increase in lignin content, which ultimately enhances the tensile strength.

On the other hand, by looking at the elongation break, it is observed that the strain is increased when the polymer was cured at low temperature. This is probably due to curing in low temperature, which makes lignin to blend with polymer instead of acting as cross linking agent and react with urethane chains. As a result, more free silanols are left to react to each other to form siloxane bonds (-Si-O-Si-). Siloxane linkages are known to be very flexible due to large bond angles and lengths, therefore acting as a soft segment in polymer network [75]. Therefore, cross link network was dominated by siloxane bond rather than lignin, resulting in increased higher flexibility. In addition, when it is cured at lower temperature, the elongation at break was increased with the increases in lignin contents. This is surprising because lignin is known to contribute to decrease in flexibility of polymer and act as hard segment in this polymer network. This can be explained by the following argument: as it is mentioned in the earlier part of the paragraph, majority of lignin tend to blend instead of reacting with urethane linkages and cross link network is dominated by siloxane bonds. In case of the polyurethane with low lignin contents, free silanols are very likely to react each other with higher probability, forming complex 3-dimensional siloxane network, ultimately forming higher cross link density. However, for the polyurethane with high lignin contents, there would be less space for free silanols to react to from 3-

dimensional siloxane network and would from linear –Si-O-Si- bridges. Therefore, polymer with higher flexibility is more likely to form a result of lower cross link density.

As it can be seen from mechanical property testing, the properties of the sustainable polyurethane can be altered from highly rigid to highly elastic by controlling the temperature and lignin content. For example, if desired product is a rigid lignin thermoplastic, then high contents of lignin should be used and cured at higher temperature in order to achieve high tensile strength.

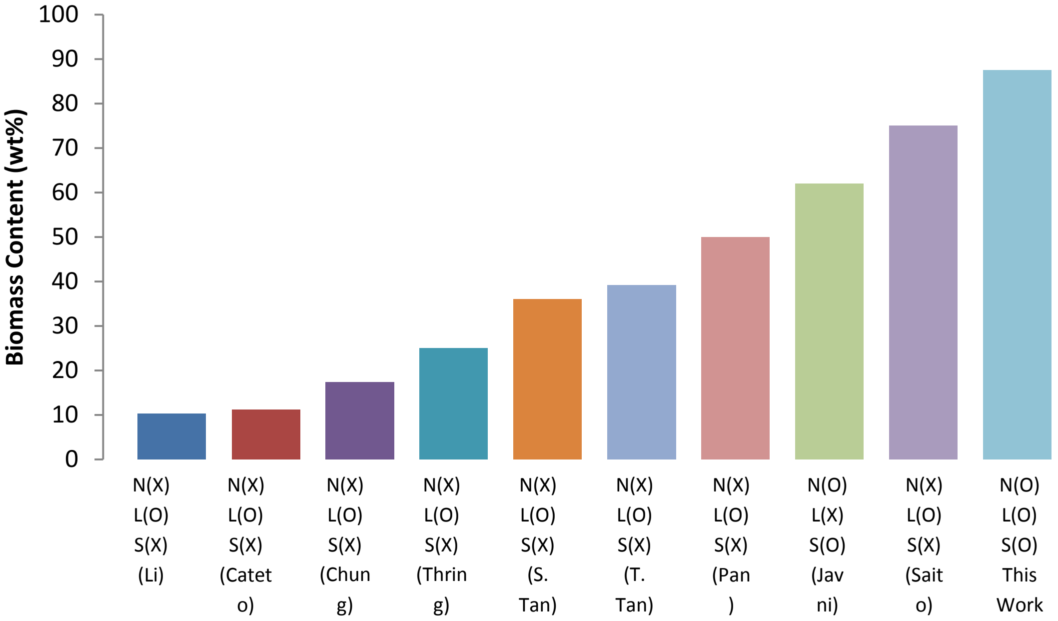


Figure 36 Biomass contents in wt % of previously reported polyurethane. L = Lignin S = Soybean Oil N = Non-Isocyanate Polyurethane

Weight percentage of biomass in our polyurethane formulation was as high as 85%. Biomass contents were compared with reported polyurethane incorporated with either soybean oil or lignin. [28, 33-34, 44-45, 74, 78-80] As it can be seen from Figure 36, our polyurethane formulation contains more biomass contents than any other sustainable polyurethane reported. Moreover, most of reported polyurethane not only contains low contents of biomass, but it is also prepared through isocyanate methods.

Also, despite Javni et al. reported non-isocyanate polyurethane with about 60% biomass contents, they had to use amine derived from petroleum based chemicals, such as ethylenediamine and butylenediamine.

5. Conclusion & Future Work

Inclusion of both soybean oil and lignin for the synthesis of sustainable polyurethane was proved to be successful, achieving biomass weight percent as high as 85% in the formulation. Moreover, addition of lignin has shown the increase of tensile strength by contributing to the rigidity of polymer and the highest tensile strength was 1.4 MPa. Also, we have shown that the weight percentage of biomass is superior to other reported lignin/soybean oil incorporated polyurethanes. This study has shown that it is feasible to synthesize non-isocyanate polyurethane which can be used as replacement for conventional isocyanate polyurethanes and successful implementation can contribute to the avoidance of the use of toxic and environmentally hazardous materials and can be performed in wide range of applications. The results suggest a broad application of polyurethane including coatings, adhesives, sealants, paintings, and elastomers.

The typical tensile strengths of processible polyurethane can vary from 1.8 – 41.0 MPa [76]; however the result shows that the highest tensile strength achieved was 1.4 MPa. Therefore, the mechanical properties need to be improved in order to make it feasible in polyurethane industry. According to Chung et al [74], lignin can be modified through demethylation and therefore have increased concentration of hydroxyl group (Figure 37). If lignin can have more hydroxyl groups, that would mean more reactive functional group to form polyurethane network with higher cross link density, resulting in higher tensile strength. This method seems to be promising in order to improve the properties of polyurethane.

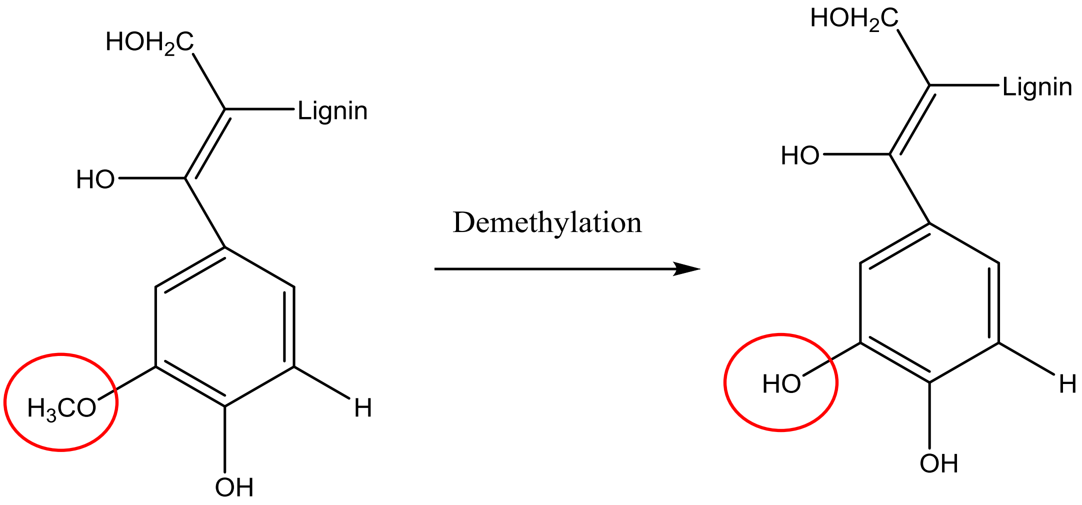


Figure 37 Demethylation of lignin

Moreover, on the other hand, this process can be further improved to become even more environmentally friendly. In this process, tetrahydrofuran(THF), which is petroleum chemical, had to be incorporated as solvent. This is due to the solubility problem of lignin, which has limited choice of solvent. We had to eliminate the use of THF and make it 100% green process, and it led us to the next step. One possible way to get rid of THF is break down of lignin into small molecule products through pyrolysis to enhance the solubility. Pyrolysis is the process that involves thermal decomposition of lignin into lower molecular weight compounds in the absence of oxygen. The schematic diagram of pyrolysis and the example of products are shown in Figure 38 [77]. Heavy oil product recovered after pyrolysis will be used as liquid state, which is likely to be miscible with APES and soybean oil; therefore the use of solvent (THF) will be unnecessary.

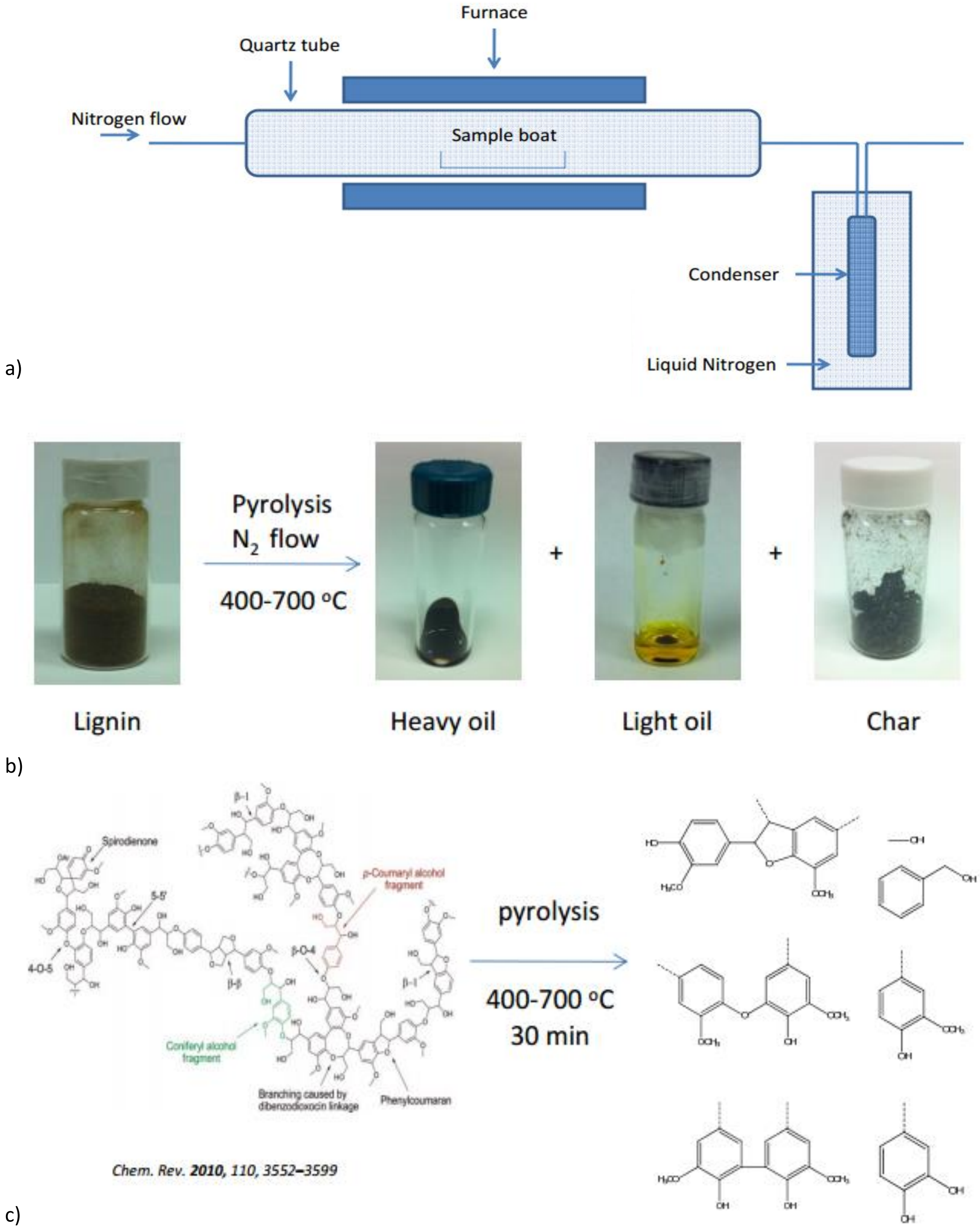


Figure 38 a) Schematic diagram of pyrolysis. The sample is decomposed in furnace and collected in condenser. b) Products of pyrolysis oil: heavy oil, light oil, char. For the future research, heavy oil will be used which contains most of the useful aromatics for polyurethane synthesis. c) Chemical structure of heavy oil after pyrolysis. Aromatic product above will be used for the synthesis of polyurethane.

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