Modification and characterization of liquefied biomass-based epoxy resin

by

Nan Wei

A thesis submitted to the Graduate Faculty of
Auburn University
in partial fulfillment of the
requirements for the Degree of
Master of Engineering

Auburn, Alabama
August 3,2013

Keywords: biomass, liquefaction, switchgrass, epoxy resin

Approved by

Yifen Wang, Co-chair, Associate Professor of Biosystems Engineering
Brian K. Via, Co-chair, Associate Professor of Forestry and Wildlife Sciences
Maria L. Auad, Associate Professor of Polymer and Fiber Engineering
Timothy P McDonald, Associate Professor of Biosystems Engineering

Abstract

With the increasing requirement of biomass composites, people have paid more attention to the increasing use of synthetic adhesives, which require petroleum-based resources. Talking about petroleum-based resources, the increased demands for energy and concerns about energy security and climate change have created more and more attention on the alternative and renewable energy which will gradually share more portion of providing energy and then replace the significant role of petroleum-based resources. Synthetic glues (urea formaldehyde/ phenol formaldehyde adhesives are the most widely utilized binders used in the wood composites industry) used in most biomass composites often contain formaldehyde, which is a toxic chemical organic substance. Therefore, we planned to develop a novel adhesive without formaldehyde. The novel adhesive will be obtained by diglycidyl ether of biphenol A (EPON 828) reacted with bio-oil which was produced by the liquefaction of biomass.

In this study, two kinds of biomass including switchgrass and southern pine wood were converted to bio-oil through a liquefaction process, and then bio-oil was utilized as a feedstock for epoxy resin synthesis. The aim of this study was to produce and characterize the liquefied biomass based epoxy resin. This study contained two main parts, one is using south pine wood as raw material for liquefaction and the other one is using switchgrass as raw material for liquefaction. And in each part, the procedure was composed of three steps, (1) liquefaction, (2) epoxidation and curing, and (3) characterization. Three different ratios of diglycidyl ether of biphenol A (EPON 828) to bio-oil (1:1, 1:2, 1:3 and 1:4) were investigated. Fourier transform-infrared spectroscopy (FT-IR) analysis proved that epoxy functionality was successfully introduced into the liquefaction oil. To determine the cure properties and thermal stability of t adhesive/cellulose composite, thermal analysis using the differential scanning calorimetry (DSC), extraction tests and thermogravimetric analysis (TGA), which were conducted.

In the first part, through the hydroxyl number tests and analyzed the residue contents, the optimal temperature and time for liquefaction were 220 °C and 2hrs. The optimal ratio of Epon 828 and southern pine wood based bio-oil was 1:1 which exhibited the highest properties in the tests of differential scanning calorimetry (DSC), extraction tests, Dynamic Mechanical analyzer (DMA) and thermogravimetric analysis (TGA). Compared to the experiment which was done by Thomas J. Robinson, he used bio-oil which used the same southern pine wood as raw material but through the pyrolysis procedure, the glass transition temperature was lower and the extraction results were also lower because the crosslink between the Epon 828 and bio-oil in this research was lower than they did.

In the second part, through the hydroxyl number tests and analyzed the residue contents, the optimal temperature and time for liquefaction were 250 °C and 2hrs. The optimal ratio of Epon 828 and switchgrass based bio-oil was 1:1 which showed the highest properties in the tests of differential scanning calorimetry (DSC), extraction tests, Dynamic Mechanical analyzer (DMA) and thermogravimetric analysis (TGA).

Acknowledgments

Firstly, I would like express my sincere gratitude to Dr. Yifen Wang (Major Advisor) for his patience and guidance on this research work during the past two years. This work would be impossible to achieve without his support. I would like to express appreciation to Dr. Brian K. Via (Co-Advisor) for his support and constructive criticisms. His enthusiastic and professional approach to research has taught me a great valuable tool for the future. Finally, I want to thank Dr. Maria L. Auad, and Dr. Timothy P. McDonald for being my committee members and for their time on reviewing my thesis. On the other hand, I need to make my honest thanks go to the members of our research group (Wei Jiang, Shuhui Wang, Bangping Wang, T. J Robinson, Celikbag Yusuf and Acquah Gifty) for their assistance in my data collection and analysis. I am also indebted to the Shanghai Ocean University, I wouldn't have made it this far without whose financial sponsorship. Lastly, I would like to thank my parents and family for all their encouragement and support throughout my entire academic career. At the end but not the least, I would like to give my enthusiastic appreciation to my boyfriend Li Ling and special friend Xiaofei Wang who gave me the most support and encouragement.

Table of Contents

List of Tables

List of Figures

List of Abbreviations

DSC	Differential Scanning Calorimetry
DMA	Dynamic Mechanical analyzer
TGA	Thermo Gravimetric Analysis
Epon 828	Diglycidyl Ether of Biphenol A
PF	Phenol formaldehyde
UF	urea formaldehyde

Chapter 1 Introduction

Renewable plant biomass resources, which include lignin, cellulose, hemicellulose and other polysaccharides, are showing significance as a suitable replacement for fossil-fuel resources. Currently, biomass from industrial residues is not effectively used, but is receiving increasing attention by society.

In the study of Jasiukaitytė et al., biomass such as wood and grass are the most important renewable natural products (Jasiukaitytė, Kunaver et al., 2010). Liquefaction of biomass can be achieved using polyhydric or phenol alcohols under specific acid as the catalyst conditions (Yamada and Ono, 2001; Rezzoug and Capart, 2002; Pan, Shupe et al., 2007; Jasiukaitytė, Kunaver et al., 2009). Phenols are a common and efficient solvent. Despite their high efficiency during liquefaction, those phenols which are not removed from the reaction waste stream could result in high pollution and higher recovery costs (Jasiukaitytė, Kunaver et al., 2010). Thus, many researchers are trying to find alternative solvents which include other multifunctional alcohols, such as glycerol, and (poly) ethylene glycol and diethylene glycol (Yamada and Ono, 2001; Kobayashi, Asano et al., 2004; Ma and Zhao, 2008; Kunaver, Medved et al., 2010).

Common adhesives used for binding all kinds of materials in the composites industry include melamine urea-formaldehyde (MUF), diphenylmethane diisocyanate (MDI), phenol formaldehyde (PF) and urea formaldehyde (UF). PF is most widely used because of its ideal mechanical properties, as well as moisture resistance, but using high volumes of these adhesives results in a depletion of petroleum-based resources. Furthermore, these synthetic adhesives contain high levels of toxins which can be harmful to humans. Human consumption of these organic substances has become problematic, and thus ways to reduce or remove formaldehyde emissions are beneficial. Consequently, one aspect of this research is to develop a novel type of adhesive without formaldehyde.

One replacement for urea formaldehyde would be epoxy resins, but it is expensive in its natural form. However, if biomass based epoxy resin (this research is using biomass through liquefaction procedure to obtain liquid biomass) could be used as a substitute during adhesive production, the resin could become more cost competitive with urea/phenol formaldehyde and reduce the possibility of dangerous formaldehyde emissions. Various biomass materials such as switchgrass, wheat straw, maize straw and wood can be utilized to make adhesives. The biomass is converted into liquid bio oil through a liquefaction procedure in most research procedures.

Liquefaction of biomass provides a chemical mixture which contains a lot of highly aliphatic hydroxyl groups. Also reactive aromatic groups can be used as reaction sites in the preparation of foams, adhesives, or other moldings; exploring a new application field in the utilization of waste wood materials. The use of liquid wood in the preparation of new polymers results in higher efficiency in the utilization of renewable resources, and act as a substitute for materials produced from crude oil.

The main objectives of this project were as follows:

Produce an oil/epoxy based thermoset which will replace the hardener part of a typical epoxy-amine type of epoxy by modification and characterization of liquefied biomass (switchgrass and southern pine wood)-based epoxy resin.

1. Obtain the optimal OH number for improved reactivity by varying liquefaction time and temperature.

2. Produce an oil/epoxy based thermoset and characterize the liquefied biomass (switchgrass and southern pine wood)-based epoxy resin for different Epon 828 to bio-oil ratios.

3. Determine the optimal ratio of Epon 828 and southern pine wood based epoxy resin for different Epon 828 to bio-oil ratios.

To achieve these objectives, the following sub objectives were carried out:

1. Produce bio oil through liquefaction using switchgrass and southern pine wood.

2. Produce high-quality resins using different ratios of bio oil reacted with Epon 828. Determine the optimal ratio of Epon and bio oil for the following chemical, mechanical, and thermal properties of the cured adhesive: solvent extraction, DMA (Dynamic Mechanical Analyzer), DSC (Differential Scanning Calorimeter), and TGA (Thermo Gravimetric Analysis).

Chapter 2 Literature Review

2.1 Energy Biomass

2.1.1 Potential of biomass for energy

In recent years, more and more attention has been placed on CO_2 emissions and the consequent correlation with global warming. Biomass is a widely available feedstock, and utilization of biomass for bioproducts can play a significant role in CO_2 reduction during manufacturing while providing a safe alternative for the environment. Hoogwijk and Faaij (et al. 2003) explored the range in biomass for energy on a global scale. They argue that, in about 50 years, the global utilization potential range of the global potential of primary biomass will be very broadly quantized at 33−1135 EJ yr^{-1}. Based on the studies which were accomplished in different countries and areas, the largest potential contribution, 0–988 EJ yr^{-1}, results from the energy crops harvested from surplus agricultural land. Given the broad availability of biomass, this feedstock for energy is anticipated to act as a large scale substitute in the near future, which could result in a depression in petroleum use. As previously reported, renewable energy sources (RES) such as biomass, hydropower, geothermal, solar, wind and marine energies supply 14% of the total world energy demand. Biomass already provided 62% of the total renewable energy sources in 1995 (Ayhan, 2005). A recent study indicated that the range of geographical potential biomass can be transformed into transportation fuels or electricity and fuel, which is equal to several times the present oil consumption (Hoogwijk, Faaij et al., 2005). Another study clarified the possibility of using straw used as biomass energy in China. China has some of the most abundant straw resources in the world and produced more than 620 million tons of straw in 2002 (Zeng, Ma et al., 2007). These studies illustrate that this energy biomass has great potential to act as a substitute for petroleum based fuel. In other previous studies, it was found that different fermentation processes, such as ethanol and methane production, could occur with acceptable waste water purification levels (Claassen, van Lier et al., 1999). It was discussed that different fermentation processes enable a more diverse utilization of biomass for gaseous and liquid biofuel applications.

2.1.2 Lignin

Lignin is an aromatic polymer which is generated by an oxidative combination by the coupling of 4-hydroxyphenylpropanoids (Vanholme, Demedts et al., 2010). Lignin can be isolated from extractive-free wood as an insoluble residue after the hydrolytic removal of polysaccharides. Alternatively, lignin can be hydrolyzed and extracted from wood, or converted to a soluble derivative. The termklason lignin is used when polysaccharides are extracted from the wood via hydrolysis with 72% sulfuric acid (Sjöström, 1993). Lignins are complex polymers that consist of phenylpropane units. Figure 1 shows that Lignin is constituted by enzymatic polymerisation of three monomers, which are coniferyl alcohol, synapyl alcohol, and p-coumaryl alcohol that lead, respectively, to guaiacyl (G), syringyl(S) and p-hydroxyphenyl propane (p-H)-type units (Fig. 2.1a). The structure of lignin is a complicated macromolecule (Fig. 2.1b) with a great variety of different kinds of functional groups and over 10 different types of linkages (Tejado, Peña et al., 2007).

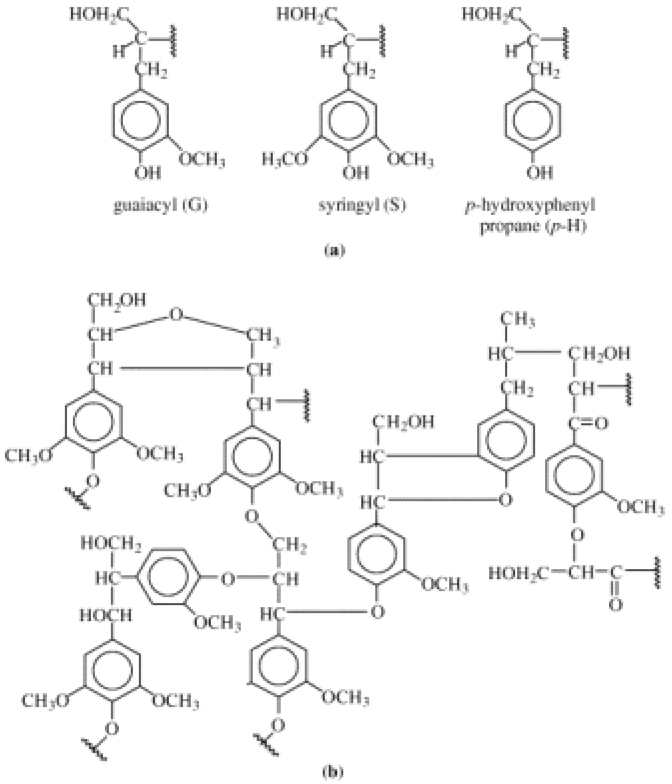
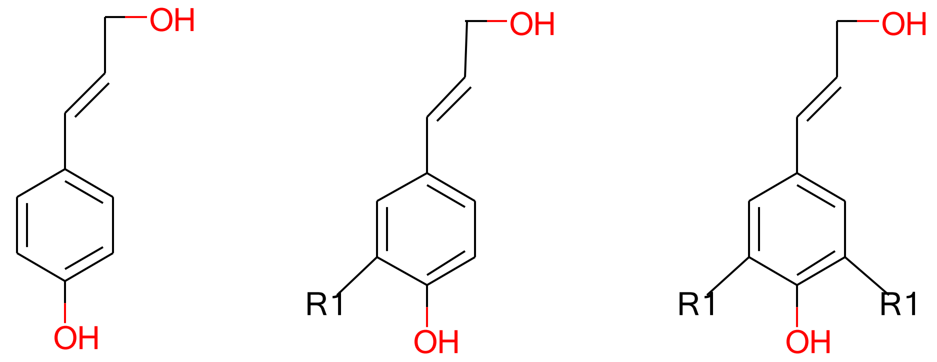


Fig. 2.1 (a) Schematic representation of the structural units of lignin, and (b) structural segment of lignin proposed by Adler (1977) (Adler, 1977).

Figure 2.2 shows the lignin precursors for plants. There are three basic lignin monomers found in lignins. Grasses and straws contain all three lignin monomers. Hardwoods contain both coniferyl alcohol (20-75%) and sinapyl alcohol (25-50%). But, softwoods contain only coniferyl alcohol. This could be used to explain the different characteristics of southern pine wood based epoxy resin and switchgrass based epoxy resin.



Grasses
P-coumaryl
alcohol

Hardwoods &
Softwood
Conlferyl alcohol

Hardwoods
Sinapyl alcohol

Figure 2.2 Lignin precursors for plants.

Here R1 means the $–OCH_3$ group.

The various hydroxyl groups experience decomposition reactions such as gasification and liquefaction that result in an increased availability of reactive groups for further applications. The biomass used in this research was switchgrass and southern pine wood. Table 1 shows the proportions of hemicelluloses/lignin/cellulose of softwoods and hardwoods and, at the same time, wheat, straw, and switchgrass for comparison (Peter, 2002).

Table 2.1

Cellulose/lignin content/hemicelluloses of selected biomass (wt %)(Peter 2002)

Biomass	Lignin (%)	Cellulose (%)	Hemi-cellulose (%)
Softwood	27–30	35–40	25–30
Hardwood	20–25	45–50	20–25
Wheat straw	15–20	33–40	20-25
Switchgrass	5–20	30–50	10–40

2.1.3 Cellulose

Cellulose is the most abundant natural polymer in wood and plants and can be extracted from industrial wastes in various forms and modifications (Abella, Nanbu et al., 2007). Approximately 45-50% of the dry substance in most wood species is comprised of cellulose with the majority of the volume located predominantly in the secondary cell wall (Mohan, Pittman et al., 2006). Some forms of lignocellulosic materials may have more cellulose than wood. Cellulose is a remarkably pure organic polymer with units of anhydroglocose held together in a long straight chain molecule. The chemical structure of cellulose is a homopolysaccharide through the linking of (1 →4) – glycosidic bonds which are composed by β-D-glucopyranose units (Fig 2.3). Two glucose anhydride units compose the basic repeating unit of the cellulose polymer which is called a cellobiose unit (Balat, Balat et al., 2009).

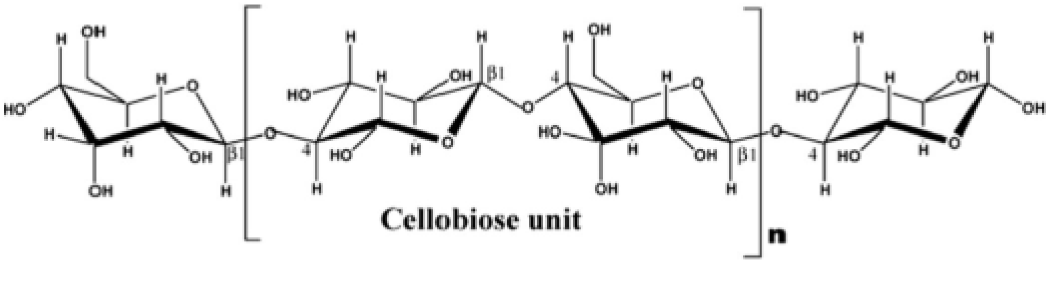


Fig. 2.3 Chemical structure of cellulose

Bundles of cellulose molecules are aggregated together in the form of microfibrils, in which highly ordered (crystalline) regions alternate with less ordered (amorphous) regions. Microfibrils build up into fibrils which further build up into cellulose fibers resulting in a natural composite matrix within the S-layer of the cell wall. As a consequence of its fibrous structure and strong hydrogen bonds, cellulose has a high tensile strength when primarily loaded axially and is insoluble in most solvents (Sjöström, 1993).

2.1.4 Hemicellulose

In contrast to cellulose, which is a homopolysaccharide, hemicelluloses are heteropolysaccharides. And like cellulose, most hemicelluloses function to connect cellulosic to lignin type polymers resulting in adequate stress transfer upon loading and consequently are important in the structural support of the cell wall (Sjöström, 1993). The amount of hemicelluloses per dry weight of wood is usually between 20 and 30% which is the second major wood chemical constituent in wood chemical composition. Here is the specific data for different kinds of wood. A variety of hemicelluloses usually account for 28% in softwoods and 35% in hardwoods (Rowell, 1984). Hemicellulose is a mixture of various polymerized monosaccharides such as mannose, galactose, arabinose, xylose, glucose 4-O-methyl, glucuronic acid, and galacturonic acid residues. Hemicelluloses (arabinoglycuronoxylan and galactoglucomammans) are related to plant gums, and exist in much shorter molecule chains than cellulose. Also, hemicelluloses exhibit lower molecular weights than cellulose. The hemicelluloses are represented in broadleaved woods as pentosans and in coniferous woods as mostly hexosanes. These polymers that consist of these sugar units are typically easily broken down in high thermal environments. Hemicelluloses are derived mainly from chains of pentose sugars and act as the adhesive material which hold the cellulose micells and fibers together (Demirbas, 2008). Formulas of the sugar component of hemicelluloses are listed in Fig 2.4(Johan Verendel, Church et al., 2011).

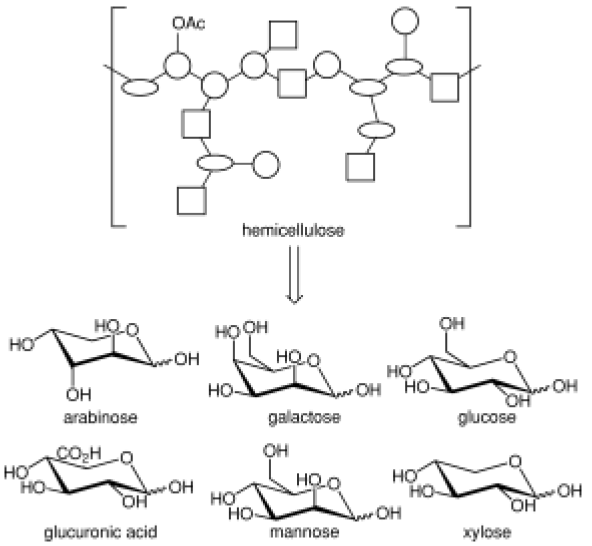


Fig. 2.4 Sugar component of hemicelluloses (Johan Verendel, Church et al., 2011)

2.1.5 Switchgrass

There are many kinds of biomass which could be transformed into the renewable bioenergy to replace the non-renewable energy such as natural gas, fuels and diesel etc. which are being consumed in increasing quantities. In the last 20 years, switchgrass utilization for non-forage purposes has increased, especially in the field of bioenergy (Parrish and Fike, 2005). In the research of the avid J. Parrish and John H. Fike, they discussed the biology and agronomy of switchgrass for biofuels and confirmed it as a potential renewable fuel source (Parrish and Fike, 2005). Switchgrass (Panicum virgatum L.) is a perennial and warm-season (C4) species grown in multiple divergent populations throughout North America. In another study, Sanderson, M. A. (et al 1996) further supported that switchgrass has the potential to be a sustainable herbaceous energy crop particularly for transportation fuel and/or biomass-generated electric power (Sanderson, Reed et al., 1996). Lemus, R. et al (2004) explored the effect of grinding performance on the physical properties of wheat and barley straws, corn stover, and switchgrass (Mani, Tabil et al., 2004). They found that switchgrass had the highest specific energy consumption (27.6 kW•ht^{-1}) among the four materials. After comparing the physical properties of grinds such as moisture content, geometric mean diameter of grind particles, particle size distribution, and bulk and particle densities were determined. They contended that switchgrass had the highest calorific value and the lowest ash content among the biomass species tested which may be related to the variation in chemical constituents. Recently, Keshwani and Cheng agreed that switchgrass is a promising feedstock for value-added applications due to its potentially low processing requirements and high productivity, for agricultural inputs and positive environmental impacts (Keshwani and Cheng, 2009). They pointed out that other value-added uses of switchgrass including gasification and liquefaction for bio-oil production and further upgrading into biobased composites, polymers and adhesives are possible.

The chemical composition and energy assessment of the switchgrass are important in determining its potential use as both a fuel and value added products such as adhesives. Table 2.2 gives a summary of the amount of cellulose, hemicelluloses and lignin present in various types of switchgrass. This data originated from the National Renewable Energy Laboratory's biomass feedstock properties and composition database (Keshwani and Cheng, 2009).

Table 2.2

Composition (% dry basis) of different switchgrass varieties from NREL's biomass feedstock composition and properties database (Keshwani and Cheng, 2009)

Switchgrass variety	Cellulose	Hemicellulose	Lignin
Alamo-whole plant	33.48	26.10	17.35
Alamo – leaves	28.24	23.67	15.46
Alamo – stems	36.04	27.34	17.26
Blackwell – whole plant	33.65	26.29	17.77
Cave-in-Rock – whole plant	32.85	26.32	18.36
Cave-in-Rock – whole plant (high yield)	32.11	26.96	17.47
Cave-in-Rock – leaves	29.71	24.40	15.97
Cave-in-Rock – stems	35.86	26.83	17.62
Kanlow-leaves	31.66	25.04	17.29
Kanolw-stems	37.01	26.31	18.11
Trailblazer	32.06	26.24	18.14

2.1.6 Southern pine wood

The biomass used for bio-oil production in this research was southern pine wood which is a widely available biomass in the southern part of the US. According to the Billion-Ton Annual Report (Perlack, Wright et al., 2005), 368 million dry tons/year of sustainable and removable biomass could be produced on existing forestlands. They estimated that nearly 1/4 of the entire annual biomass population could be used from forest and agricultural resources to supply bioenergy and bioproduct processes (Perlack, Wright et al., 2005).

2.2 Liquefaction of biomass

According to Xianyang Zeng (2007), technologies which have been polularized and commercialized in China such as direct biogas, combustion, straw gasification, and straw briquetting have the potential for being environmentally friendly while providing an adequate supply of rural energy. But other technologies, including straw carbonization, liquefaction and bio-coal, have been underutilized. Despite their low cost and technical feasibility, they are currently being developed slowly (Zeng, Ma et al., 2007). Liquefaction is anticipated to play a significant role in the global energy sector due to the simplicity of the reagent and operation, as well as environmentally friendly process. According to Rezzoug and Capart (2002), the process of wood liquefaction occurs in two steps: a) ethylene-glycol or other pure or recycled solvents are used as a wood solvent and b) high pressures are utilized to provide catalytic hydrogenation and solvolysis to produce a liquid product. In the first step of their experiment, they used ethylene glycol and sulphuric acid with a 4:1 and 0.01:1 ratio to the biomass, respectively, obtain the bio-oil successfully. The temperature of the reactor was raised at a rate of 3℃/min and then kept at a plateau of 250℃. From these results, we know that the chemical composition of liquefied cellulose strongly depends on the liquefying conditions such as time and temperature. For cellulose, the rate of depolymerization has been found to be a limiting factor which drives the time to liquefaction (Kobayashi, Asano et al., 2004). Furthermore, they suggested that the condensation reaction was attributable to the mutual reaction between degraded aromatic derivatives from lignin and depolymerized cellulose, or because of the nucleophilic displacement reaction of cellulose by phenoxide ion. Others have characterized the residues after liquefaction using wet chemical analyses, fourier transform infrared (FTIR) spectroscopy, x-ray diffraction (XRD), and scanning electron microscopy (SEM)(Pan, Shupe et al., 2007). Three different ratios of phenol to wood by weight were explored and ranged from 1/1 to 3/1. These 3 ratios were complimented by three other experimental variables including liquefaction temperature, phenol/wood ratio, and cooking method. It was found that each factor played a significant role in the composition of the residues. Table 2.3 represents a comprehensive review of the different parameters that could be used during liquefaction to generate bio-oil.

Table 2.3 Different methods of the biomass liquefaction

Liquefaction materials	Reagent	Ratio(based on biomass) (w/w)	Temperature (℃)	Time	Resource
Pine wood chips	Ethylene glycol Sulphuric acid	4/1 0.01/1	250	Changing	(Rezzoug and Capart, 2002)
Commercial cellulose, Lignocellulosics (Sawdust of white birch)	EG 97% sulfuric acid	5/1 0.15/1	150°C	Changing	(Yamada and Ono, 2001)
White birch, Cellulose powder, Alkali lignin, Steamed lignin	Glycerol Polyethylene glycol Sulfuric acid	0.3/1 1.5/1 0.15/1	150°C	Changing	(Kobayashi, Asano et al., 2004)
Wood powder	Phenol Oxalic acid	1/1 - 3/1 0.05/1 -	150°C 180°C	3 hrs	(Pan, Shupe et al., 2007)

		0.15/1			
Lignocellulosic waste (sawdusts of white birch, Japanese cedar, and Japanese cypress)	EC, PC 97% sulfuric acid	5/1 0.15/1	150°C	Changing	(Yamada and Ono, 1999)
Cellulose	EC PTSA MSA	5/1 changing changing	Changing	Changing	(Sung Phil Mun, 2001)
Bagasse	EC	-	140–170 °C	0-18 mins	(Xie and Chen, 2005)
Corn stover Wheat straw Rice straw	EG EC` Polyethylene glycol+ glycerol(9/1) EC+ EG(8/2) 97% sulfuric acid	10/3 10/3 10/3 10/3 10/3	160°C	Changing	(lingyun liang, 2006)
Spruce and fir sawdust	Glycerol+ DEG(4/1, w/w) PTSA	3/1 0.09/1	150°C	4 hrs	(Jasiukaitytė, Kunaver et al., 2010)
Meals (poplar, oak, spruce and beech)	Glycerol+DG (4/1 w/w) p-toluenesulfonic acid	3/1 0.09/1	180°C	3 hrs	(Kunaver, Medved et al., 2010)

Where ethylene carbonate (EC)

Propylene carbonat (PC)

Ethylene glycol (EG)

Methanesulforic acid (MSA)

Diethylene glycol (DEG)

P-toluene sulphonic acid (PTSA)

2.3 Basic introduction of general Epoxy resin

Epoxy resin is a polymer which is formed from two different chemicals. The basic chemistry of the adhesive system involves a diepoxide and a polyfunctional amine, which will lead to a crosslinked system upon curing. The diepoxide is usually derived from Bisphenol A and epichlorohydrin. A simple diglycidyl derivative of Bisphenol A or oligomeric compounds with epoxide end groups could then be produced through tightly controlled reaction conditions. The hardener consists of polyamine monomers such as triethylenetetramine (TETA). When these compounds are mixed together, the amine groups will react with the epoxide groups to form a covalent bond. When each NH group can react with one epoxide group, the resulting polymer is heavily crosslinked and thus has high rigidity and strength. The most common and significant type of epoxy resins is formed from reacting epichlorhydrin with bisphenol A to produce bisphenol A diglycidyl ethers. The simplest resin of this type is formed from reacting two moles of epichlorhydrin with one mole of bisphenol

A to produce the bisphenol A diglycidyl ether. Figure 2.5(a) shows the basic structure of bisphenol-A diglycidyl ether epoxy resin. Curing may be achieved by reacting an epoxy with itself (homopolymerization) or by forming a copolymer with polyfunctional curatives or hardeners. In principle, any molecule containing reactive hydrogen may react with the epoxide groups of the epoxy resin. Common classes of hardeners for epoxy resins include amines, acids, acid anhydrides, phenols, alcohols, and thiols. Figure 2.5(b) shows the structure of TETA which is a typical hardener. The amine (NH2) groups react with the epoxide groups of the resin during polymerization.

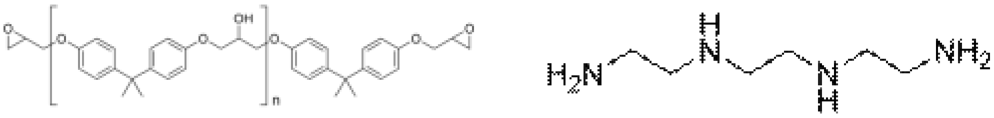


Figure 2.5 (a) Structure of bisphenol-A diglycidyl ether epoxy resin

(b) Structure of TETA

2.3.1 Wood-based epoxy resin

In recent years, researchers have paid great attention to the optimization of epoxy resin mechanical and thermal properties. It has been found that an epoxy resin can be toughened using synthesized polyurethane prepolymer based on hydroxyl-terminated polyesters (Harani, Fellahi et al., 1998). They added either a rigid phase or a rubbery phase to improve epoxy resin toughness. Hajeme Kimura et al. (1998) investigated the epoxy resin cured by bisphenol-A based benzoxazine. This alternative epoxy resin system was found to exhibit good water resistance, electrical insulation, heat resistance, and mechanical properties. W.J. Wang et al. (2000) further investigated the characterization and properties of new silicone-containing epoxy resin and found that they could synthesize a new epoxy monomer, triglycidyloxy phenyl silane (TGPS) with competitive properties. This new epoxy system exhibited a high limiting oxygen index which resulted in superior flame resistance, making it available for harsh temperature environments. These studies all demonstrate that the system can be engineered through various reaction mechanisms and reactants to result in a wide array of applications which make it a suitable system for new product development. There appears to be future opportunities which involve exploring new methodologies such as adding filler, injecting new components such as substitutes for petroleum, reinforcing elements, plasticizer, and dialing in the final performance of the epoxy resin system through changes in synthesis reactants and processing procedures.

To date, most biobased epoxy systems have focused on the substitution of lignin, which is a cross-linked phenylpropanoid polymer; whereas literature on pyrolysis or liquefaction into bio-oil (as a substitute) has been more limited. Lignin and bio-oil type systems should respond similarly in the mechanism of reaction since bio-oil has similar polyphenolic type structures. But the rate and magnitude of reaction may differ since bio-oil has smaller sized molecules resulting in more available OH sites. Hence, the next section of this review will focus more on lignin-based epoxy resin which has been extensively studied and has been shown to maintain or improve adhesive thermal and mechanical properties. It is also more friendly to the environment and often cheaper since lignin can be obtained from pulp and paper or bioenergy waste streams. In the research of Delmas et al., wheat straw Biolignin™ was used as a substitute of bisphenol-A in epoxy resin. Synthesis was carried out in alkaline aqueous media using polyethyleneglycol diglycidyl ether (PEGDGE) as epoxide agent (Delmas, Benjelloun-Mlayah et al. 2013). In the study of Kishi et al., wood-based epoxy resins were synthesized from resorcinol-liquefied wood (Kishi, Fujita et al. 2006).

Hirose, S et al. investigated the synthesis and thermal properties of epoxy resins from ester-carboxylic acid derivative of alcoholysis lignin (Hirose, Hatakeyama et al., 2003). Hajime Kishi et al. (2006) discussed the synthesis of wood-based epoxy resins and their mechanical and adhesive properties. In their study, wood was first liquefied in the presence of resorcinol both with or without a sulfuric acid catalyst, and at a high temperature. They found that the wood-based epoxy resins would be well suited for the matrix component of natural plant-fiber reinforced composites.

2.3.2 Test Methods of Adhesive

There are many methods which are used to evaluate the properties of the adhesive. A great number of studies have focused on how to characterize epoxy resin properties. For example, Deng, Hu et al. (1999), investigated the curing reaction and physical properties of DGEBA/DETA epoxy resin blended with propyl ester phosphazene. They used DSC (Differential Scanning Calorimeter), SEM, DMA (Dynamic Mechanical Analyzer), TGA (Thermo Gravimetric Analyzer) and tensile testing to investigate the thermal and strength performance of the epoxy prepolymer. Furthermore, in most studies, most thermal and mechanical properties could be measured with dynamic differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Dynamic Mechanical Analyzer (DMA) (Park and Jin, 2004). From the above researches, it is evident that DSC, SEM, DMA, tensile testing, and

TGA are the common approaches to evaluate the properties of epoxy resin.

2.3.2.1 Dynamic Differential Scanning Calorimetry (DSC)

The objective of calorimetry is to measure the heat of the reaction during curing and consequent crosslinking. In order to measure heat, the heat needs to be exchanged. The exchanged heat can be used as a measure of the heat exchanged which is affected by a temperature change in a system, or the heat flow created in the heat exchange process, leading to temperature differences, could be a measure indicator of the heat flow along its path. Caloric measurements have been carried out since the middle of the 18th century. Now, the modern Differential Scanning Colorimeter (DSC) is widely used today (Höhne, Hemminger et al., 2003). Several studies have been conducted to determine the enthalpy of pyrolysis for a biomass sample.

DSC is a method which could be used to determine the heat required to trigger a reaction which results in crosslinking of the polymer. As the cross-linked network develops, it either releases or absorbs heat depending of the nature of the reaction. This heat flow with change in temperature can then be plotted to understand the crosslinking behavior. More specifically, the shape of the DSC curve is: the Y-axis is the endothermic or exothermic rate of the sample. In other words, it is the heat flow rate (dH / dt) (units millijoules / sec) in which the temperature (T) forms the X-axis. This analytical tool can thus be beneficial in the characterization of polymer thermodynamic and kinetic parameters. For example, specific heat capacity, heat of reaction, the heat of transition, the phase diagram, reaction rate, rate of crystallization, the degree of crystallinity of polymers, and sample purity can all be calculated or estimated from the enthalpy behavior of the system. In this research, the main purpose of the DSC is to determine the glass transition temperature of different bio-based epoxy resins. Several studies have been conducted to determine the endothermic and exothermic performance of different material samples. Tao Xie et al. employed DSC to determine the thermal properties of epoxy resin from the liquefied product which is liquefied with the bagasse in ethylene carbonate (Xie and Chen, 2005). They found that the resin presented higher adhesive shear strength and better thermal stability than a commercial epoxy resin. In the study of Hui Pan et al., they measured the cure kinetic mechanisms of the LWPF resins with dynamic and isothermal differential scanning calorimetry (Pan, Shupe et al., 2008). They found that the isothermal DSC data indicated that the cure reactions of both resins followed an autocatalytic mechanism. The activation energies of the liquefied wood resins were close to that of a reported lignin–phenol–formaldehyde resin but were higher than that of a typical phenol formaldehyde resin. In this research, Differential Scanning Colorimeter Q2000 was used to measure the heat of the reaction during curing and consequent crosslinking. Refrigerated cooling system, 90 and Tzero sample press, and pans are all from TA Instruments Company.

2.3.2.2 Thermo Gravimetric Analyzer (TGA)

Thermo gravimetric analysis is a technique used to determine the weight loss of a material when it is subjected to high temperatures at a controlled rate in a nitrogen or air environment. The machine used for this technique is a Thermo Gravimetric Analyzer (TGA). In this study, Thermo Gravimetric Analyzer (TGA) Q500 from TA

Instruments Company was employed to examine the degradation temperature.

2.3.2.3 Dynamic Mechanical Analyzer (DMA)

Dynamic Mechanical Analyzer is a technique used to study and characterize materials. The most useful function is to study the viscoelastic behavior of polymers. A sinusoidal stress is applied giving rise to strain in the measure. The strain is measured and monitored to assist in the complex calculation of modulus. The temperature of the sample or the frequency of the stress is often varied, resulting in a change in the modulus. This technique can help determine the glass transition temperature of the material and can identify transitions attributed to molecular motions. In the research of Joo Ran Kim et al. (2012), the thermal experiments were conducted using the dynamic mechanical analyzer (DMA) to determine the extent of the resin conversions and their thermal transitions into a thermoset matrix.

2.3.2.4 Fourier Transform Infrared Spectroscopy Machine (FT-IR)

Fourier transform infrared (FT-IR) spectroscopy is a rapid, noninvasive technique with considerable potential to rapidly identify the presence or disappearance of key functional groups as a result of different reactions or treatments (Ellis, Broadhurst et al., 2002). In the research of Pan et al. (2008), they employed FT-IR to determine the presence of key functional groups associated with liquefied wood. In the studies of Hui Pan et al. (2007); T. Yamada et al. (1999); Joo Ran Kim et al. (2011), FT-IR was used to monitor specific peaks of the residue after various liquefaction treatments (Yamada and Ono, 1999; Pan, Shupe et al., 2007; Kim and Sharma, 2012).

2.4 Reference

Abella, L., S. Nanbu, et al. (2007). "A theoretical study on levoglucosan pyrolysis reactions yielding aldehydes and a ketone in biomass."

Adler, E. (1977). "Lignin chemistry—past, present and future." Wood Science and Technology **11**(3): 169-218.

Ayhan, D. (2005). "Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues." Progress in Energy and Combustion Science **31**(2): 171-192.

Balat, M., M. Balat, et al. (2009). "Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems." Energy Conversion and Management **50**(12): 3147-3157.

Claassen, P. A. M., J. B. van Lier, et al. (1999). "Utilisation of biomass for the supply of energy carriers." Applied Microbiology and Biotechnology **52**(6): 741-755.

Demirbas, A. (2008). "The Importance of Bioethanol and Biodiesel from Biomass." Energy Sources, Part B: Economics, Planning, and Policy **3**(2): 177-185.

Denq, B.-L., Y.-S. Hu, et al. (1999). "The curing reaction and physical properties of DGEBA/DETA epoxy resin blended with propyl ester phosphazene." Journal of Applied Polymer Science **74**(1): 229-237.

Ellis, D. I., D. Broadhurst, et al. (2002). "Rapid and Quantitative Detection of the Microbial Spoilage of Meat by Fourier Transform Infrared Spectroscopy and Machine Learning." Applied and Environmental Microbiology **68**(6): 2822-2828.

Höhne, G., W. F. Hemminger, et al. (2003). Differential scanning calorimetry, Springer.

Harani, H., S. Fellahi, et al. (1998). "Toughening of epoxy resin using synthesized polyurethane prepolymer based on hydroxyl-terminated polyesters." Journal of Applied Polymer Science **70**(13): 2603-2618.

Hirose, S., T. Hatakeyama, et al. (2003). "Synthesis and thermal properties of epoxy resins from ester-carboxylic acid derivative of alcoholysis lignin." Macromolecular Symposia **197**: 157-169.

Hoogwijk, M., A. Faaij, et al. (2005). "Potential of biomass energy out to 2100, for four IPCC SRES land-use scenarios." Biomass and Bioenergy **29**(4): 225-257.

Hoogwijk, M., A. Faaij, et al. (2003). "Exploration of the ranges of the global potential of biomass for energy." Biomass and Bioenergy **25**(2): 119-133.

Jasiukaitytė, E., M. Kunaver, et al. (2010). "Lignin behaviour during wood liquefaction—Characterization by quantitative 31P, 13C NMR and size-exclusion chromatography." Catalysis Today **156**(1–2): 23-30.

JOHAN VERENDEL, J., T. L. Church, et al. (2011). "Catalytic One-Pot Production of Small Organics from Polysaccharides." Synthesis(11): 1649-1677.

Keshwani, D. R. and J. J. Cheng (2009). "Switchgrass for bioethanol and other value-added applications: A review." Bioresource Technology **100**(4): 1515-1523.

Keusch, S. and R. Haessler (1999). "Influence of surface treatment of glass fibres on the dynamic mechanical properties of epoxy resin composites." Composites Part A: Applied Science and Manufacturing **30**(8): 997-1002.

Kim, J. R. and S. Sharma (2012). "The development and comparison of bio-thermoset plastics from epoxidized plant oils." Industrial Crops and Products **36**(1): 485-499.

Kimura, H., A. Matsumoto, et al. (1998). "Epoxy resin cured by bisphenol A based benzoxazine." Journal of Applied Polymer Science **68**(12): 1903-1910.

Kishi, H., A. Fujita, et al. (2006). "Synthesis of wood-based epoxy resins and their mechanical and adhesive properties." Journal of Applied Polymer Science **102**(3): 2285-2292.

Kobayashi, M., T. Asano, et al. (2004). "Analysis on residue formation during wood liquefaction with polyhydric alcohol." Journal of Wood Science **50**(5): 407-414.

Kunaver, M., S. Medved, et al. (2010). "Application of liquefied wood as a new particle board adhesive system." Bioresource Technology **101**(4): 1361-1368.

lingyun liang, Z. M. (2006). "liquefaction of crop residues for polyol production."

Mani, S., L. G. Tabil, et al. (2004). "Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass." Biomass and Bioenergy **27**(4): 339-352.

Melvin G.R, C. (2003). "Carbon sequestration and biomass energy offset: theoretical, potential and achievable capacities globally, in Europe and the UK." Biomass and Bioenergy **24**(2): 97-116.

Mohan, D., C. U. Pittman, et al. (2006). "Pyrolysis of Wood/Biomass for Bio-oil: A

Critical Review." Energy & Fuels **20**(3): 848-889.

Pan, H., T. F. Shupe, et al. (2007). "Characterization of liquefied wood residues from different liquefaction conditions." Journal of Applied Polymer Science **105**(6): 3740-3746.

Pan, H., T. F. Shupe, et al. (2008). "Synthesis and cure kinetics of liquefied wood/phenol/formaldehyde resins." Journal of Applied Polymer Science **108**(3): 1837-1844.

Park, S.-J. and F.-L. Jin (2004). "Thermal stabilities and dynamic mechanical properties of sulfone-containing epoxy resin cured with anhydride." Polymer Degradation and Stability **86**(3): 515-520.

Parrish, D. J. and J. H. Fike (2005). "The Biology and Agronomy of Switchgrass for Biofuels." Critical Reviews in Plant Sciences **24**(5-6): 423-459.

Perlack, R. D., L. L. Wright, et al. (2005). Biomass as feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply, DTIC Document.

Peter, M. (2002). "Energy production from biomass (part 1): overview of biomass." Bioresource Technology **83**(1): 37-46.

Rezzoug, S.-A. and R. Capart (2002). "Liquefaction of wood in two successive steps: solvolysis in ethylene-glycol and catalytic hydrotreatment." Applied Energy **72**(3–4): 631-644.

Rowell, R. M. (1984). The chemistry of solid wood, ACS Publications.

Sanderson, M. A., R. L. Reed, et al. (1996). "Switchgrass as a sustainable bioenergy crop." Bioresource Technology **56**(1): 83-93.

Sjöström, E. (1993). Wood chemistry: fundamentals and applications, Academic Pr.

Sung Phil Mun, E.-B. M. H., Tae Ho Yoon (2001). "evaluation of organic sulfonic acids as catalyst during cellulose liquefaction using ethylene carbonate." Industrial Engeering Chemistry **7**: 430-434.

Tejado, A., C. Peña, et al. (2007). "Physico-chemical characterization of lignins from different sources for use in phenol–formaldehyde resin synthesis." Bioresource Technology **98**(8): 1655-1663.

Vanholme, R., B. Demedts, et al. (2010). "Lignin Biosynthesis and Structure." Plant

Physiology **153**(3): 895-905.

Wang, W. J., L. H. Perng, et al. (2000). "Characterization and properties of new silicone-containing epoxy resin." Polymer **41**(16): 6113-6122.

Xie, T. and F. G. Chen (2005). "Fast liquefaction of bagasse in ethylene carbonate and preparation of epoxy resin from the liquefied product." Journal of Applied Polymer Science **98**(5): 1961-1968.

Yamada, T. and H. Ono (1999). "Rapid liquefaction of lignocellulosic waste by using ethylene carbonate." Bioresource Technology **70**(1): 61-67.

Yamada, T. and H. Ono (2001). "Characterization of the products resulting from ethylene glycol liquefaction of cellulose." Journal of Wood Science **47**(6): 458-464.

Zeng, X., Y. Ma, et al. (2007). "Utilization of straw in biomass energy in China." Renewable and Sustainable Energy Reviews **11**(5): 976-987.

Zhao, B. Y., G. Chen, et al. (2001). "Synthesis of lignin base epoxy resin and its characterization." Journal of Materials Science Letters **20**(9): 859-862.

Chapter 3

Modification and characterization of liquefied southern pine wood based epoxy resin

3.1 Introduction

It is essential that industrial systems consider factors that may be contributing to global-warming and the eventual depletion of fossil fuels. Utilization of plant biomass for bioenergy and bioproducts is one way to offset carbon emissions because it recycles carbon instead of supplementing carbon from fossil fuels (Kishi, Fujita et al., 2006). Because carbon can be sequestered at the same rate as it is released during manufacturing, it can be classified as a renewable resource which will ensure a sustainable but functional and technological planet for generations to come. Therefore, people have invested much effort into finding ways to use biomass as a renewable feedstock during polymer and chemical processing.

Wood is one of the most significant natural resources. Wood is an orthotropic material due to it complex organization of wood chemistry, fiber morphology, and macro characteristics such as earlywood and latewood formation (Jasiukaitytė, Kunaver et al., 2009). Lignin, cellulose and hemicelluloses are the three main components in wood chemical structure. During liquefaction, hemicellulose and cellulose are removed while lignin which has a smaller molecular weight is retained. This is the principal reaction component in the liquefaction process, and it generates an aromatic polymer which is generated by an oxidative combination by the coupling of 4-hydroxyphenylpropanoids (Vanholme, Demedts et al., 2010). Lignin can be isolated from extractive-free wood as an insoluble residue after hydrolytic removal of the polysaccharides. Alternatively, lignin can be hydrolyzed and extracted from wood or converted to a soluble derivative. Figure 3.1 (a) and (b) show the basic structure of lignin.

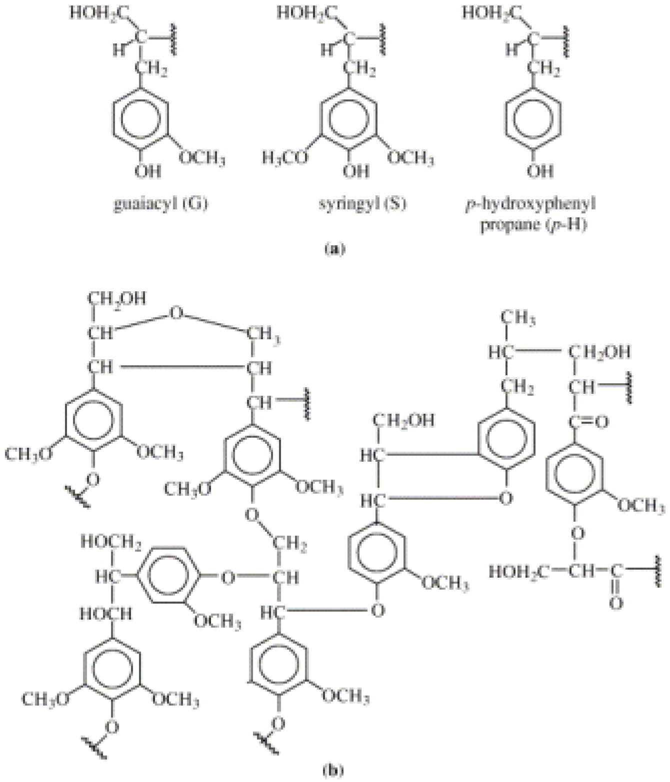


Fig. 3.1 (a) Schematic representation of the structural units of lignin, and (b)Structural segment of lignin proposed by Adler (1977)(Adler, 1977).

In this research, the principal material to generate bio-oil is southern pine wood. It will be used as raw materials to produce bio-oil via liquefaction. However, in addition to the natural unzipping of lignocellulosic polymers during high temperature exposure (Via et al., 2013) the depolymerization of the macromolecular structure during liquefaction results in the interaction and reaction of specific organic reagents and specific catalysts to the biomass substrate. The resulting phenolic rich but diverse bio-oil can then be used as a new feedstock for polymer production (Yamada and Ono, 2001; Rezzoug and Capart, 2002; Kobayashi, Asano et al., 2004). The depolymerization of wood components can be obtained with polyhydric or phenol alcohols under acid-catalyzed conditions. Liquefied wood has a high reactivity due to the large amount of phenolic OH groups and alcoholic OH groups (Jasiukaitytė, Kunaver et al., 2009; Jasiukaitytė, Kunaver et al., 2010; Kunaver, Medved et al., 2010). Using these functional groups, liquefied wood can be converted to polyurethane forms and phenolic resins (Tan, 1996; Nonaka and Tomita et al., 1997; Zhao, Chen et al., 2001). Liquefied wood has further potential and may be used as a resource for other valuable biomass-based materials. The epoxy-resin family has good mechanical and adhesive performance, and is widely used in various fields such as adhesives, coatings, and matrix resins of composites. The first objective of this study is to synthesize southern pine wood based epoxy resins using liquefied southern pine wood as the precursor for resin production. The second objective is to evaluate the mechanical, thermal, and adhesive properties of the wood-based epoxy resins in order to clarify its potential for a suite of applications. In the research of H.P.S Abdul Khalil et al. (2011), they generated the use of EFB-lignin as a curing agent in epoxy resin, as shown in the reaction scheme in Figure 3.2

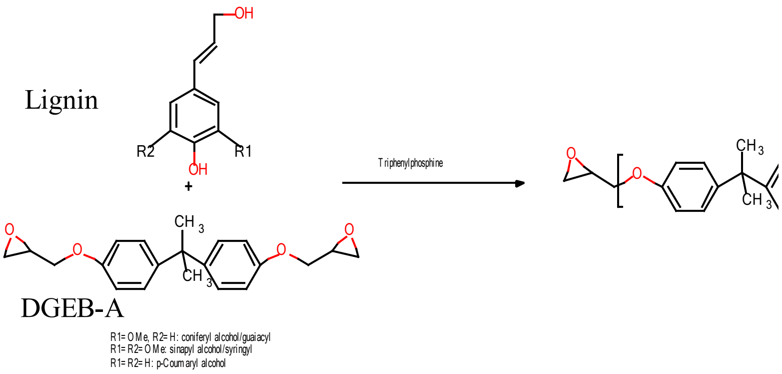


Fig. 3.2 Idealized network formation during curing reaction of epoxy-lignin system (Abdul Khalil, Marliana et al., 2011)

In the study of Maria L. Auad et al. (2011), they mainly focused on the development and optimization of the processing methodology to produce epoxy modified phenolic foams. They also analyzed the relationship between the composition and the structure as well as the mechanical and flammability performance of epoxy-phenolic (E-P)-based foams, as shown in reaction scheme in Figure 3.3 (Maria L. Auad, Zhao et al., 2007). The epoxy they used was Epon 826 and the hydroxyl group supplier was Novolac which were Epon 828 and southern pine wood based bio-oil. They have similar reaction theory to produce epoxy resin.

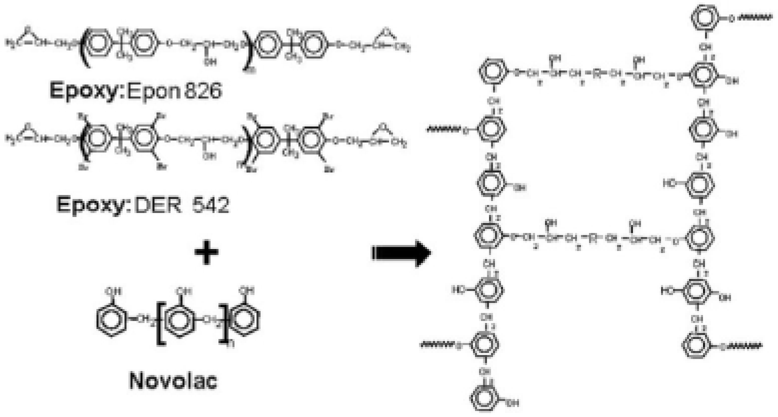


Fig.3.3 Schematic of the E-P systhesis reaction (Maria L. Auad, Zhao et al., 2007)

When all of the results were analyzed, we found that the optimal liquefaction temperature was 220℃when the time was fixed at 2h. Then we fixed the liquefaction temperature at 220℃, and changed the liquefaction time as to 1h, 2h, and 3h. We found the optimal liquefaction time by various tests including residue content collection of liquefaction residue, hydroxyl number test, pH value of bio-oil, and the thermal properties tests of southern pine wood based epoxy resin.

3.2 Materials and Methods

The following are flow charts Figure 3.4 of how to optimize the liquefaction temperature when liquefaction time was fixed at 2hrs and Figure 3.5 of how to optimize the liquefaction time when liquefaction temperature was fixed at 220^{o}C.

Fig. 3.4 Flow chart of optimizing the liquefaction temperature when the liquefaction time was fixed at 2hrs.

Figure 3.5 Flow chart of optimizing the liquefaction time when the liquefaction temperature was fixed at 220°C.

3.2.1. Biomass (southern pine wood) Preparation

A hammer mill (New Holland grinder model 358, New Holland, PA.) with 3.175-mm (1/8 in.) sieve size was used for particle size reduction. Particles from southern pine wood (Panicum virgatum) were collected and oven-dried at 105℃ for 12hrs and kept in a desiccator at room temperature before use. The dried material was ground to pass through a 20 mesh sieve before placing it in the oven. Diethylene glycol (99%, from Alfa Aesar chemical company) was used as the reagent solvent during liquefaction. All other chemicals for liquefaction of southern pine wood and modification of wood-based epoxy resins were of reagent grade and were used without further purification.

3.2.2 Liquefaction of southern pine wood

The liquefaction procedure of southern pine wood was based on the general method described by Tao Xie (Xie and Chen, 2005), and then subsequently modified by Matjaž Kunaver (Kunaver, Medved et al., 2010). The liquefaction of southern pine was carried out free of pressure in a 1000 ml three neck glass reactor equipped with a mechanical stirrer (500 rpm) and reflux condenser device. The reactor was charged with 100g of wood and 400g of diethylene glycol and then was heated to the desired temperature for liquefaction. One g of 98% sulfuric acid was added and the mixture was heated for various times (1h, 2h and 3h) at various temperature (200℃, 220℃, 240℃, 250℃ and 260℃) while being constantly stirred.

3.2.2.1 Determination of residue content

The residue content evaluation method used in this work was a modification of the method described by Hui Pan et al. (Pan, Shupe et al., 2008) and Hajime Kishi et al (Kishi, Fujita et al., 2006). The liquefied mixture was diluted with 500 mL of acetone and vacuum-filtered with Whattman #1 filter paper three times to separate the dissolved southern pine wood particle residue and the solved portion. The insoluble residues was put into oven to be dried at 105℃±2℃ for 24 hrs and stored in a desiccator. The residue content of the liquefied wood was calculated by eq. (1):

$$\text{Residue Content } (\%) = W_R/W_O \times 100 \qquad (1)$$

Where W_R is the oven-dried weight of the solid southern pine wood residue after the filtration and W_O is the weight of the original southern pine wood particles (Pan, Shupe et al., 2007). The residue content was defined as the percent dry weight of the acetone insoluble substance of the total biomass charged. Usually, it is used as an index for the extent of liquefaction.

3.2.2.2 Hydroxyl group number test

The hydroxyl group number of the liquefaction product is defined as the mass of KOH equivalent to that of the phthalic anhydride consumed in the phthalification of 1 g of the sample. The hydroxyl number was measured according to ASTM D4274-11. Fresh and dry pyridine and standard 0.5 N and 0.1 N sodium hydroxide solutions, were used for all reactions. First, 111 to 116 g of phthalic anhydride was weighed in a 1000 mL brown bottle. Then, 700 mL of pyridine was added, which had been distilled from phthalic anhydride, and the bottle was shaken vigorously until it was dissolved. The reagent was stored must stand overnight at room temperature before use. The samples were added to the pressure bottles. Then, 25 mL of the phthalic anhydride reagent was then accurately pipetted into each of the bottles. The following formula (2) was used to determine the amount of sample needed for the hydroxyl reaction:

Sample size = 561/estimated hydroxyl number (2)

The bottles were capped and the samples were placed closely together with the cap on the bottles. The samples and blanks were kept as close together as possible in a water bath which was maintained at 98 ± 2 ℃ for 2h. Then the bottles were removed and allowed to cool to room temperature. Once cooled, 50 mL of redistilled pyridine and 0.5mL of the phenolphthalein indicator solution were added and then titrated with standard 0.5 N NaOH solutions to a pink end point that persists for at least 15s. Due to the dark coloration of the liquefied oil, a pH determination for future sample titration was made from blanks reacted in triplicate. The following equation (3) was used to calculate the hydroxyl group number from the results of titration values.

Hydroxyl number = [(B-A) N×56.1]/W + acid number, mg KOH/g (3)

Where, A is the volume of the 0.5M sodium hydroxide solution required for the titration of the sample (mL); B is the volume of the sodium hydroxide solution required for the titration of the blank solution (mL); N is the molarity of the sodium hydroxide solution; and W is the amount of the sample (g) to be analyzed.

If the sample contains significant acidity or alkalinity, the result must be corrected. An amount of sample equal to that taken previously for the hydroxyl determination was weighed into a 400 mL Erlenmeyer flask. Then, 75 mL of redistilled pyridine, 75 mL of distilled water, and 0.5 mL of phenolphthalein indicator solution was added to the flask. The samples were then titrated with standard 0.1 N sodium hydroxide solution to a pink end point that persisted for at least 15s. Because of the dark coloration of the liquefied oil, a pH determination for future sample during titration was made from blanks and reacted in triplicate. The following equation (4) was used to calculate acid number.

Acid correction (mg KOH/g) = [(C-B) N×56.1]/W (4)

Here, C is the titration volume of the potassium hydroxide solution (mL); B is the titration volume of the blank solution (mL); N is the normality of the sodium hydroxide solution; and W is the weight of sample used.

3.2.2.3 PH value examination

A Fisher Scientific AR 20 pH/Conductivity Meter was employed for determining the Ph value of the bio-oil.

3.2.2.4 Interaction in liquefaction using FT-IR

The method to determine the interaction between Epon 828 and bio-oil in the liquefaction method used in this work was a modification of the method described by Kimura Hajime et al. (Kimura, Matsumoto et al., 1998). The Fourier Transform Infrared (FT-IR) analysis of the liquefied wood residues was performed by an attenuated total reflectance ATR FT-IR spectrometer (PerkinElmer, model Spectrum 400). A small amount of residue was applied directly on the diamond crystal and a constant force and time duration (± X) between samples was applied. Data was acquired using the FT-IR software Spectrum from 500cm^{-1} to 4000cm^{-1}.

3.2.3 Preparation of southern pine wood based epoxy resin

Epon 828 and liquefied wood Epon 828 were mixed until fully homogenized at ratios of 1:1 to 1:4 at one part increments. Triphenylphosphine was added into the mixture as 3% of the amount of Epon 828 as a catalyst. Tetrahydrofuran was added into the mixture to reduce the viscosity of the bio-based epoxy resin which makes the mixture easier to mix until homogeneous. The samples for the following tests were prepared by pouring the Epon 828 and bio-oil mixture into aluminum weighing dishes (10cm diameter). The curing temperature ramp is 30 mins at 80℃, 30 mins at 105℃, 2 h at 150℃, 1 h at 180℃, and 1 h at 200℃. After the curing process, the samples were left in the oven to cool down slowly in order to remove the bubbles in the samples.

3.2.4 Analytical methods

3.2.4.1. Measurement of glass transition temperatures

The results of Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analyzer (DMA) helped to optimize the ratio of EPON 828 to bio-oil by measuring the glass transition temperature for each ratio during polymer crosslinking. Measurements of the glass-transition temperature and the cure reaction of the wood based epoxy resin were performed on a TA Differential Scanning Calorimetry (DSC) Q2000 calorimeter. In order to measure the glass-transition temperature, about 4-10 mg of southern pine wood based epoxy resin was placed into an aluminum sample pan and sealed with a lid by Tzero sample press. An empty pan and a lid of the same type were used as a reference. The temperature of DSC was programmed first from the room temperature to -20℃ and increased from -20℃ to 300℃ at 20℃/min to eliminate the effect of water that might exist in the sample (Pan, Shupe et al., 2007). The sample was then heated to 250℃ at the same rate. Dynamic Mechanical Analyzer (DMA) measured the glass-transition temperature of various southern pine wood based samples by employing the Dynamic Mechanical Analyzer (DMA) Instrument RSA3, TA Instruments.

3.2.4.2 Measurement of Thermal Degradation

A thermal gravimetric analyzer (TA Instruments TGA Q500) was employed to measure the thermal degradation of the wood based epoxy resin after polymerization. About 7-10 mg of resin powder was placed into a sample pan, and the degradation reaction was conducted within a nitrogen atmosphere where the temperature was increased from ambient temperature to 800℃ at a heating rate of 10.00 °C/min.

3.2.4.3 ATR FT-IR characterization of Epon to bio-oil interaction FT-IR

The Fourier Transform Infrared (FT-IR) analysis of the liquefied southern pine wood residues was performed by an FT-IR spectrometer (PerkinElmer, model Spectrum 400). A small amount of biobased epoxy resin was applied directly on the diamond crystal. A constant force and time duration (± X) between samples was applied. Data was acquired using FT-IR software spectrum.

3.2.4.4 Crosslink characterization performed by Soxhlet extraction tests

As the degree of crosslinking decreases, weight loss of the polymer upon solvent exposure should increase and is thus a sensitive measure to determine the optimum ratio of Epon to bio-oil. The southern pine wood based epoxy resin was milled to 20 meshes. Afterward, the samples were placed into an oven at 105℃ and left overnight to remove the moisture, weight the weight of the cellulose tube w_r and the total weight of cellulose tube plus sample weight which was w_o. Then the ground sample was placed into the extraction device which as shown in the figure 3.6, 150 mL of acetone was then added into the extraction tube The soxhlet and acetone was refluxed and the extraction test was ran for 4hrs. After 4 hrs, the obtained the sample was removed from the extraction tube and placed into a fume hood where the flow rate was 224, where the acetone was evaporated off. The sample and cellulose thimble were then placed into a vacuum oven to remove the rest of acetone at 40℃ for 24 hrs. The sample plus cellulose tube was weighed and recorded as w_d. The equation to calculate the extractive content is as follows:

Non-extractive content (%) = $(w_o - w_d) / (w_o - w_r) \times 100$

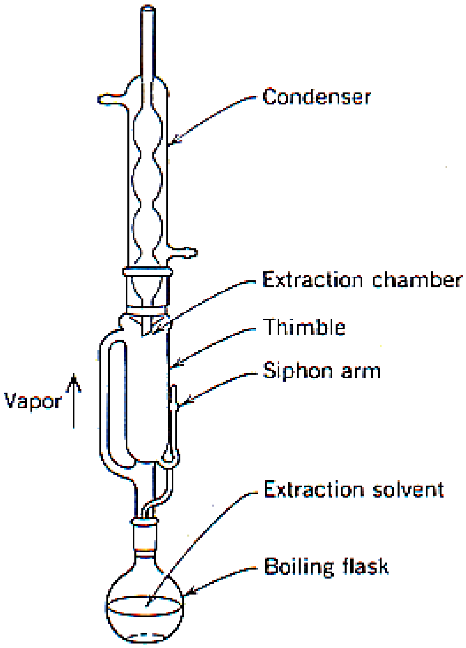


Fig. 3.6 The Soxhlet extraction system

3.2.5 Data Analysis

All analysis of data sets and plotting of graphs were performed using Origin 8.0 software (Version 8.0, OriginLab Corporation, Microcal Software).

3.3 Results and Discussion

3.3.1 Residue content of liquefied southern pine wood

Figure 3.7 (a) and (b) show the residue contents of liquefied southern pine wood with varying temperatures and times. With the increasing of the temperature, the residue of the liquefaction of southern pine wood had the tendency to decrease. The minimum residue content was obtained at 220°C. However, the residue content tended to increase when the temperature reached 240°C. The results indicate that temperature has a great influence on the liquefaction efficiency. It seems that enhancing the temperature promotes the degradation of southern pine wood fibers at a relatively low temperature, and it showed the recondensation of degraded fragments at a high temperature. However, a further increase in the temperature could promote the recondensation of the reaction intermediate, so the residue content tended to increase. In the research of Xie and Chen, they reported the similar tendency that the residue content decreased as the temperature increased at the low temperature. However, the residue content increased as the temperature increased at high temperature (Xie and Chen 2005). Through the Figure 3.7 (a) and (b) indicate that a longer liquefaction time was not better because the liquefaction time that was 2 h had the lowest residue content.

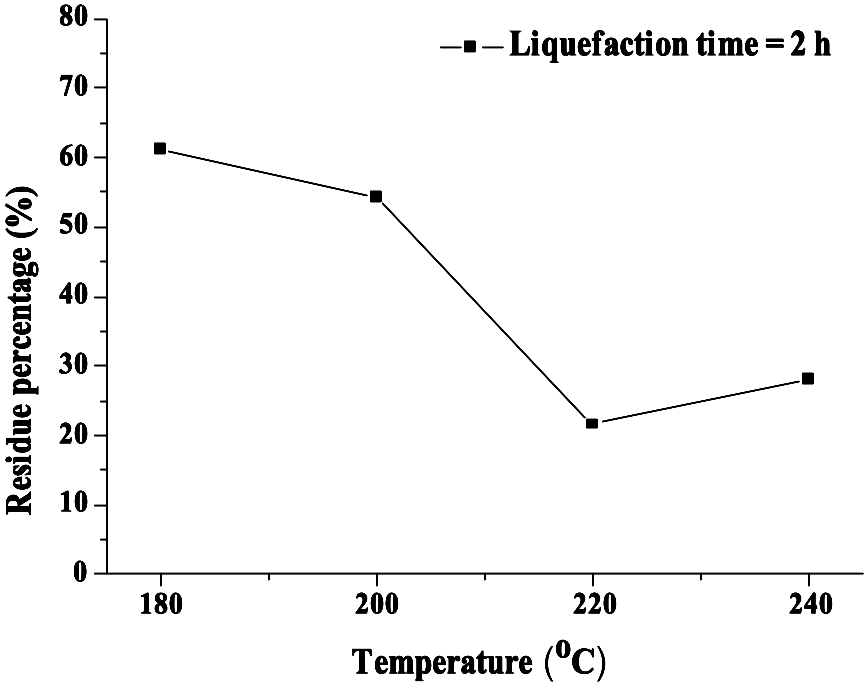


Fig. 3.7 (a) Relationship between the liquefaction temperature and residue percentage.

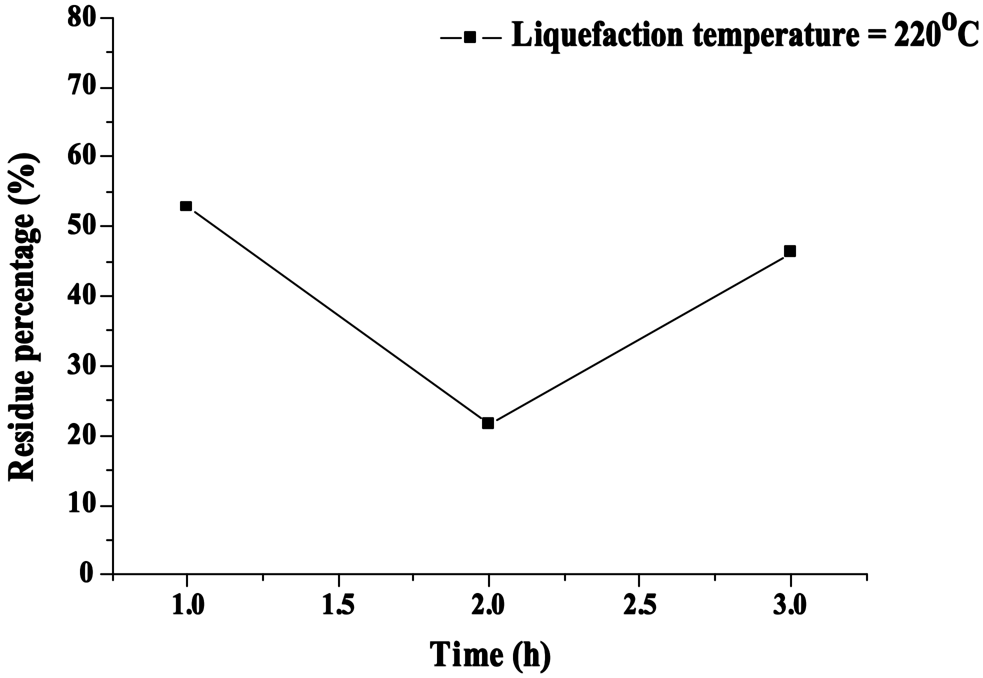


Fig. 3.7 (b) Relationship between the liquefaction time and residue percentage.

3.3.2 Hydroxyl number and pH value of liquefied southern pine wood

The hydroxyl group content is one of the most important factors of relevance when calculating reactant ratios in condensation reactions (Kurimoto, Doi et al., 1999). As shown in Figure 3.8 (a) and (b), the OH group number for each sample was taken at different liquefaction time and temperatures. As the temperature increased, the hydroxyl group number decreased in a nonlinear fashion. This decrease in hydroxyl groups, along with increased temperature, may be attributed to the dehydration and thermal oxidation of the diethylene glycols as well as the condensation reactions between the glycols and main wood components such as cellulose, hemicelluloses, and especially lignin (Kunaver, Medved et al., 2010). In the research of Yao et al. (1996), they subjected glycols alone to the same liquefaction conditions and measured the hydroxyl group number. They found that the hydroxyl group numbers of the glycols did not change significantly which indicated that the main decrease in hydroxyl group numbers of the reaction mixture was due to the reactions between the main wood components such as lignin, cellulose and hemicelluloses and the glycols that were present.

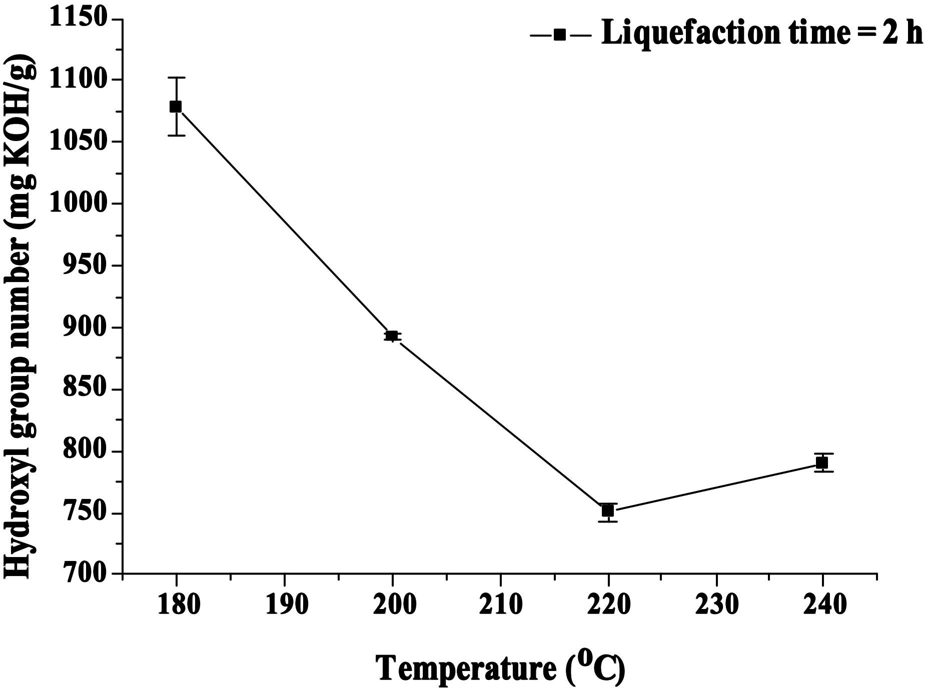


Fig. 3.8 (a) Relationship between the liquefaction temperature and the hydroxyl group number.

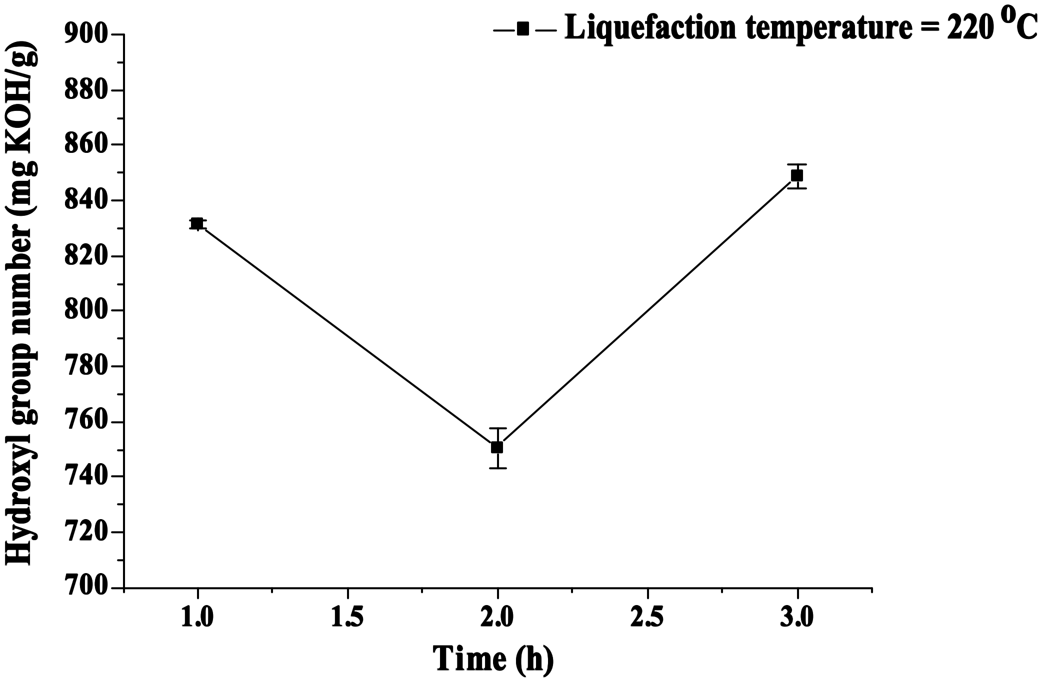


Fig. 3.8 (b) Relationship between the liquefaction time and the hydroxyl group number.

There was no specific pH value tendency when the liquefaction temperature was changed from 180°C to 240°C, and the highest pH value occurred when the liquefaction temperature was 200°C. When the liquefaction time was changed from 1h to 3 h, the lowest pH value was observed at 2 h.

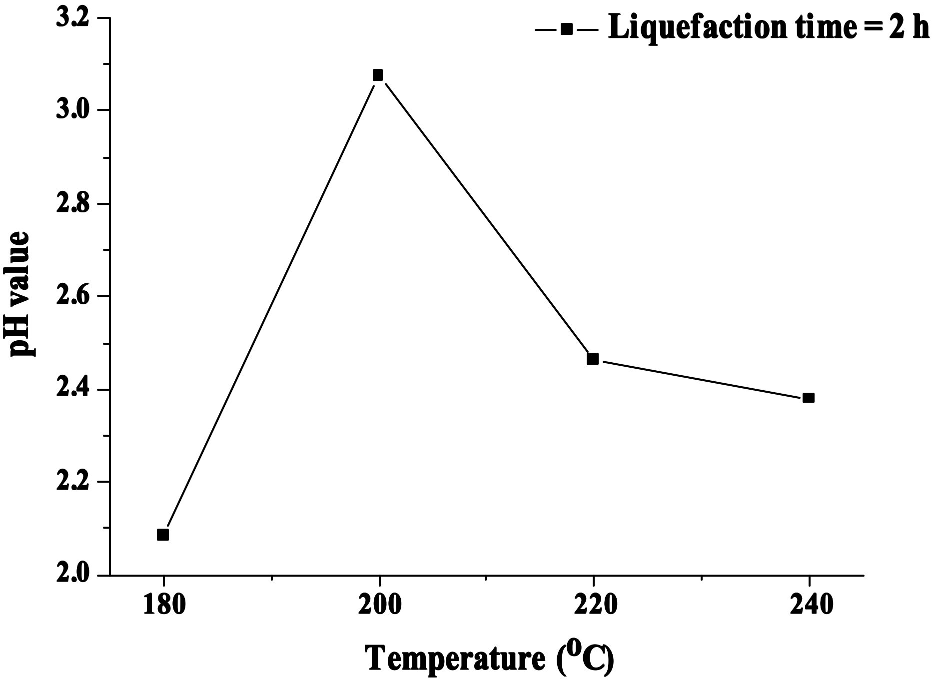


Fig. 3.9 (a) Relationship between the liquefaction temperature and pH value.

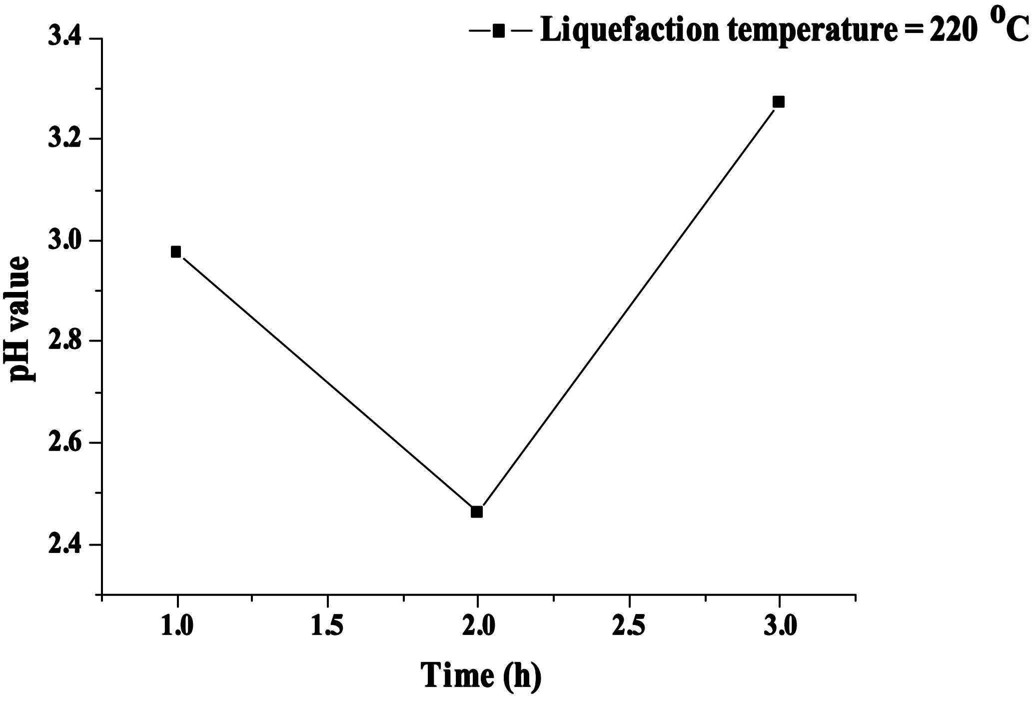


Fig. 3.9 (b) Relationship between the liquefaction time and pH value.

3.3.3 Differential Scanning Calorimeter (DSC)

A differential scanning calorimeter was used in studying the glass transition temperature of the wood based epoxy resins. The nature, liquefaction conditions and ratios of Epon 828 to southern pine wood based bio-oil before running samples through the DSC had an effect on the results. The results from the DSC run are presented in Figure 3.10 and Figure 3.11. Table 3.1 shows the specific glass transition temperature of each sample. The different synthesis conditions show endothermic cure peaks similar to each other. The sample with 220°C as a liquefaction temperature and 1:1 as synthesis ratio of Epon 828 to pine wood based epoxy resin had the highest glass transition temperature. This indicates that the degree of crosslinking in this sample was the highest. And the ratio 1:1 (Epon 828: wood based bio-oil) was the optimal ratio for the productions epoxy resin. The liquefaction temperature at 220°C was the optimal temperature for liquefaction.

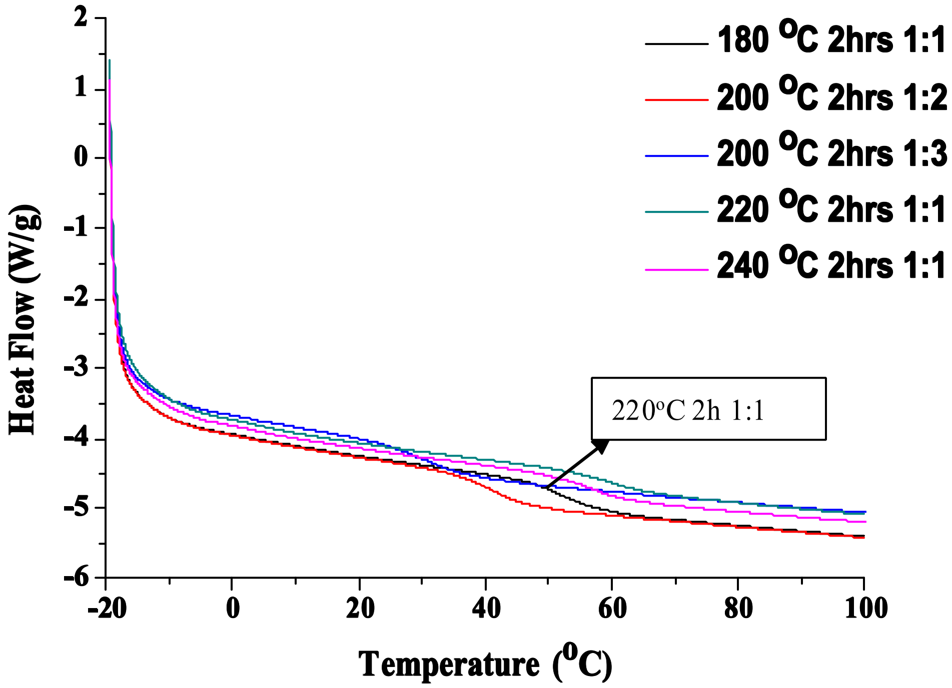


Fig. 3.10 DSC results of different sample in different liquefaction temperature and ratio of Epon 828 to southern pine wood based bio-oil.

Table 3.1 Specific DSC results of different sample in different liquefaction temperature and ratio of Epon 828 to southern pine wood based bio-oil.

"-" means the status of the test samples were too rubbery to be tested.

Temperature	Mass ratio Epon 828 : Bio-oil			
	1:1	1:2	1:3	1:4
180	52.44	-	-	-
200	-	40.84	30.91	-
220	59.73	-	-	-
240	55.06	-	-	-

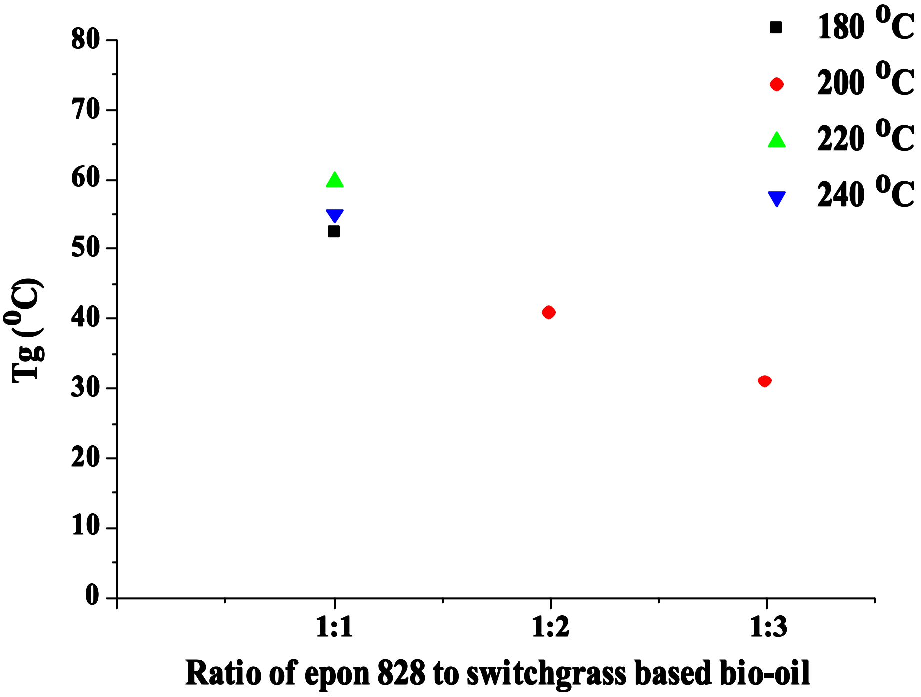


Figure 3.11 Specific DSC results of different sample in different liquefaction temperature and ratio of Epon 828 to southern pine wood based bio-oil.

The following Figure 3.12, Figure 3.13 and Table 3.2 indicate that the optimal liquefaction time was 2 h and the optimal ratio of southern pine wood based bio-oil was 1:1 because it had the highest glass transition temperature, 59.73°C. This indicates that the degree of crosslinking in this sample was the highest.

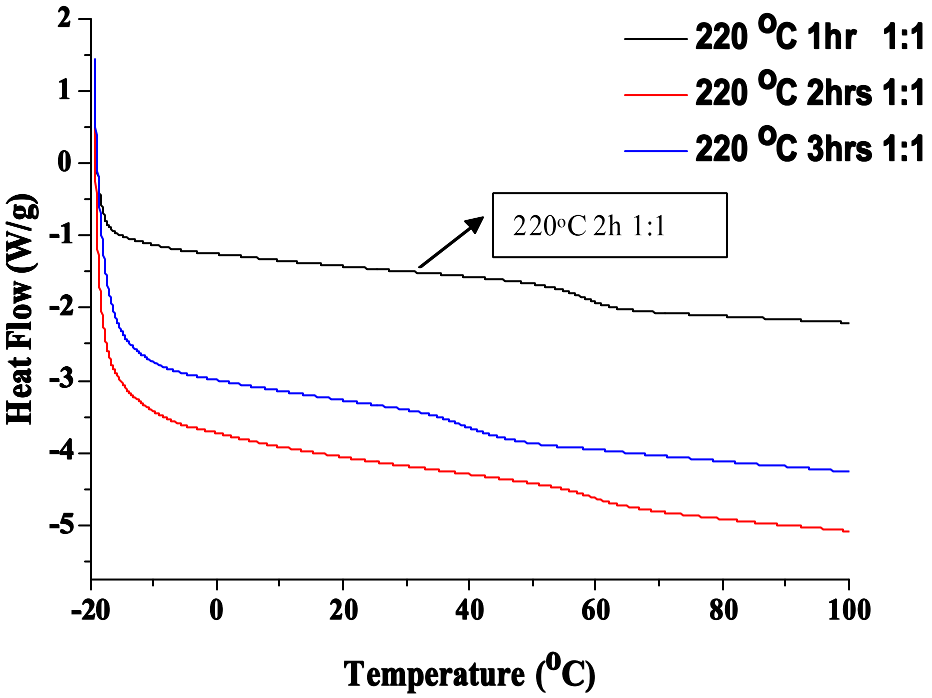


Fig. 3.12 DSC results of different samples in different liquefaction time and ratio of Epon 828 to southern pine wood based bio-oil.

Table 3.2 Specific DSC results of different sample in different liquefaction time and ratio of Epon 828 to southern pine wood based bio-oil.

"-" means the status of the test samples were too rubbery to be tested.

Time (h)	Mass ratio Epon 828 : Bio-oil			
	1:1	1:2	1:3	1:4
1	57.18	-	-	-
2	59.73	-	-	-
3	-	38.52	-	-

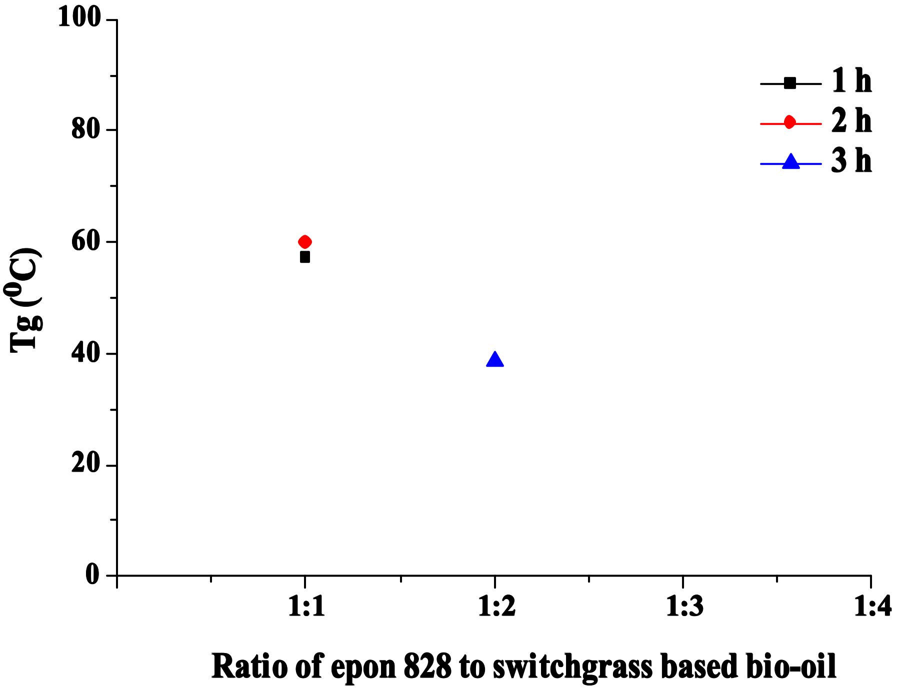


Figure 3.13 Specific DSC results of different samples in different liquefaction time and ratio of Epon 828 to southern pine wood based bio-oil.

3.3.4 Thermo Gravimetric Analyzer (TGA)

In the TGA figures, two different decomposition temperatures 380°C and 540°C were observed to represent the primary peaks associated with wood based epoxy resin degradation in Figure 3.14 and Figure 3.15. This is similar to Chen et al. (2008) who observed three overlapping peaks at 245˚C, 418°C and 545°C in the DTG (Derivative Thermogravimetric) curves for a commercial resol PF adhesive. The first temperature peak in this research was 380°C which was attributed to the stage where methylene bridges decompose or are broken into methyl groups. The degradation of phenols occurs in the second stage which is 540°C. In first stage, 220°C was the liquefaction temperature and 2 h was the liquefaction time and the mass ratio of Epon 828 to southern pine wood based bio-oil was 1:1. Consequently, the first stage had the highest degradation temperature. The second temperature peak in this research was 530°C according to literature, and in this research was 540°C. The results obtained from the TGA thermograms in the second degradation stage showed that when the liquefaction temperature was 240°C, fixed liquefaction time was 2 h, and the mass was 1:1, the highest degradation temperature was attained.

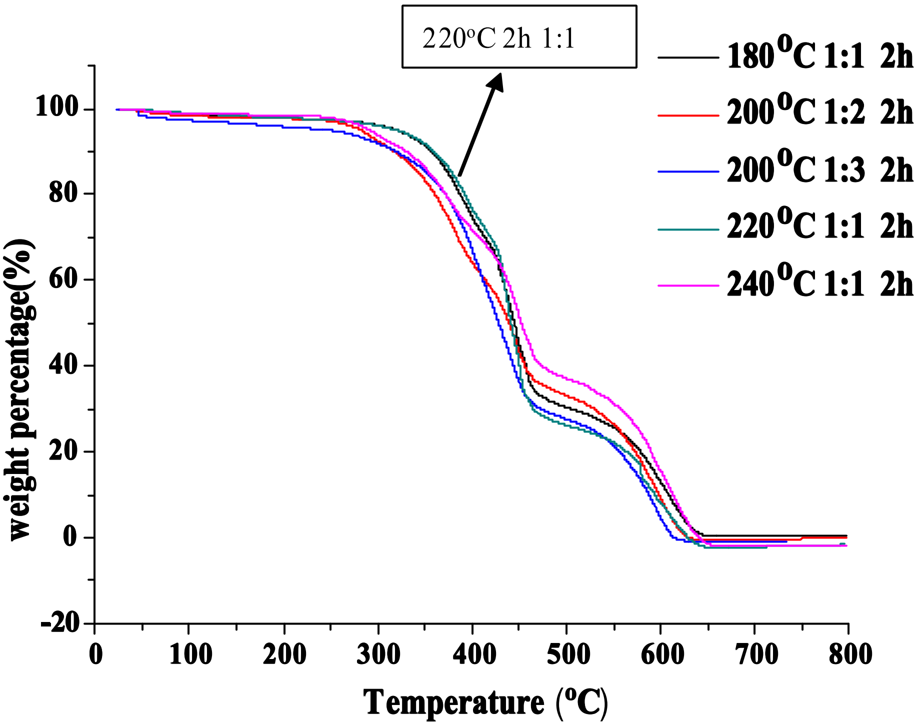


Fig. 3.14 Thermogravimetric (TG) curves for southern pine wood based epoxy resins when liquefaction time was fixed at 2 h and liquefaction temperature was changed from 180°C to 240°C.

From Figure 3.15, when the liquefaction temperature was 220°C, and fixed liquefaction time was 2 h, and the mass ratio of Epon 828 to southern pine wood based epoxy resin was1:1, the epoxy resin had the highest degradation temperature in the first degradation stage which indicates the higher thermal stabilities of the southern pine wood based epoxy resin. When the liquefaction temperature was 220°C and liquefaction time was 1 h, and the mass ratio of Epon 828 to southern pine wood based epoxy resin was 1:1, the epoxy resin had the highest degradation temperature. The results of TGA also proved that the optimal liquefaction temperature was 220°C and optimal liquefaction time was 2h.

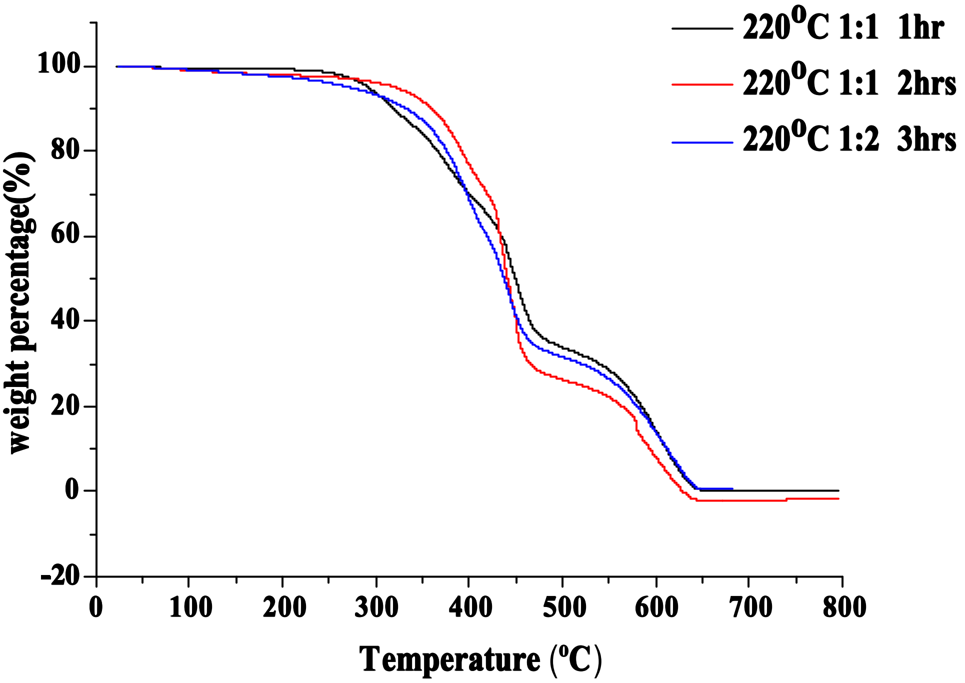


Fig. 3.15 Thermogravimetric (TG) curves for southern pine wood based epoxy resins when liquefaction temperature was fixed at 220°C and liquefaction time was changed from 1 h to 3 h.

3.3.5 Extraction tests

In order to determine the solubility, which in turn can give an indication of the crosslinking volume of the wood based epoxy resin, extraction tests in acetone were run. The optimal ratio of Epon 828 to Bio-oil, which was more stable, has a higher percentage of crosslinking within the network structures. After 4 h of extraction, the minimum ratio was 1:4 which is illustrated in Table 3.3 and Figure 3.16.

Table 3.3 The Acetone Soxhlet extraction tests of southern pine wood based epoxy resin at different liquefaction temperature.

"-" means the status of the test samples were too rubbery to be tested.

Temperature (°C)	Mass ratio of Epon 828 to Bio-oil							
	1:1		1:2		1:3		1:4	
	Avg(%)	SD	Avg (%)	SD	Avg(%)	SD	Avg(%)	SD
180	23.10	0.26	-	-	-	-	-	-
200	-	-	45.93	0.83	-	-	-	-
220	18.64	0.42	-	-	-	-	-	-
240	37.81	0.76	-	-	-	-	-	-

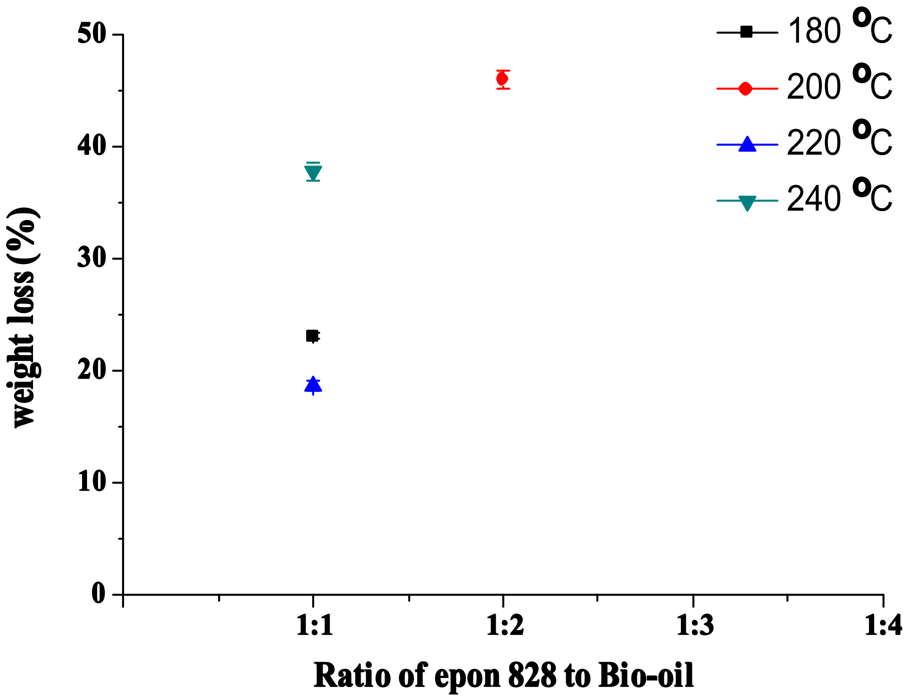


Figure 3.16 The acetone Soxhlet extraction tests of southern pine wood based epoxy resin at different liquefaction temperature.

The results of the acetone Soxhlet extraction tests of wood based epoxy resin in different liquefaction temperatures are presented in Table 3.4 and Figure 3.16. The change in the mass loss of different samples, which used changing temperature in the liquefaction processes and the changing ratios of Epon 828 to Bio-oil in epoxidation reaction, give an indication of the optimal ratio of Epon 828 to Bio-oil which is 1:1, and the weight loss of this sample was lowest at 18.64. This showed that the degree of crosslinking in the epoxy resin sample was highest for the 1:1 ratio.

Table 3.4 The Acetone Soxhlet extraction tests of southern pine wood based epoxy resin at different liquefaction time.

"-" means the status of the test samples were too rubbery to be tested.

Time (h)	Mass ratio of Epon 828 to Bio-oil							
	1:1		1:2		1:3		1:4	
	Avg (%)	SD	Avg(%)	SD	Avg(%)	SD	Avg (%)	SD
1	72.33	0.42	-	-	-	-	-	-
2	18.64	0.42	-	-	-	-	-	-
3	-	-	41.09	0.50	-	-	-	-

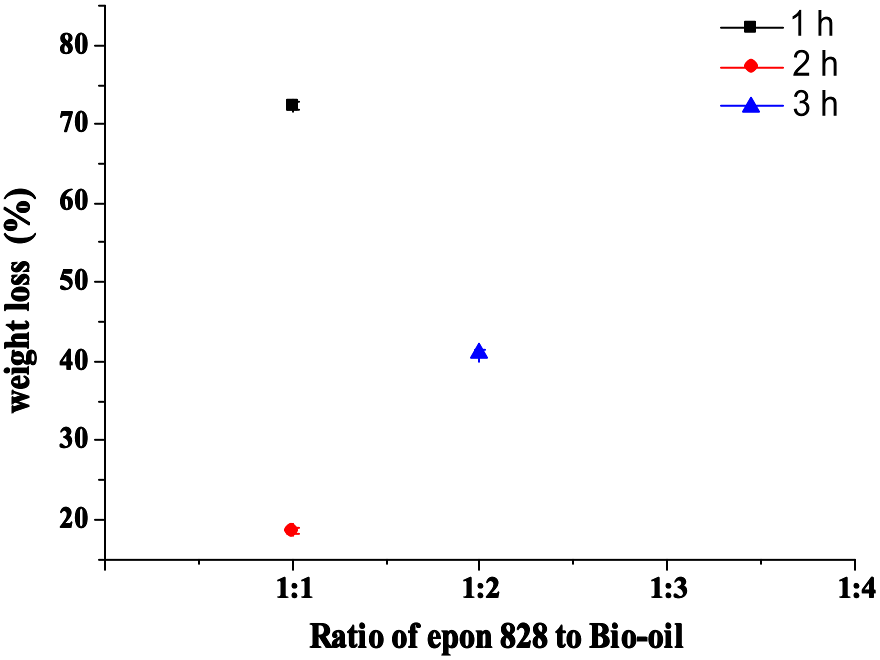


Figure 3.17 The acetone Soxhlet extraction tests of southern pine wood based epoxy resin at different liquefaction time.

From the Table 3.4 and Figure 3.17, the lowest mass loss was resulted from the same sample in which the reaction conditions included ratio of Epon 828 to Bio-oil was 1:1, liquefaction time was 2hrs, and the liquefaction temperature was fixed at 220°C.

3.3.6 FT-IR spectroscopy

The composition of polymeric materials can be determined by measuring their infrared spectra using a Fourier transform infrared (FT-IR) spectrometer and then comparing the results with a commercially available or specifically prepared spectral data base. FT-IR identifies types of chemical bonds (functional groups) present in bio-oil or bio-based epoxy resin. The absorbance of light at a given wavenumber is a function of the underlying chemical bonds within the system. By interpreting the infrared absorption spectrum, the presence of a chemical bond in a molecule can be determined; likewise, the consumption efficiency of reactants can be used to determine the optimal ratio. FT-IR was used to examine possible interactions between pine wood, Epon 828, and bio-oil.

From Figure 3.18, a broad absorption band at 3354cm^{-1} was assigned to aromatic and aliphatic OH groups (Abdul Khalil, Marliana et al. 2011) which disappeared in the FT-IR curve of southern pine wood based epoxy resin. This means that we successfully produced Hydroxyl groups and the OH group reacted with Epon 828 to generate the new type of southern pine wood based epoxy resin. The characteristic stretching vibration of the peroxide moieties at 914 cm^{-1} (C-O-C), completely disappeared after curing (Abdul Khalil, Marliana et al. 2011).

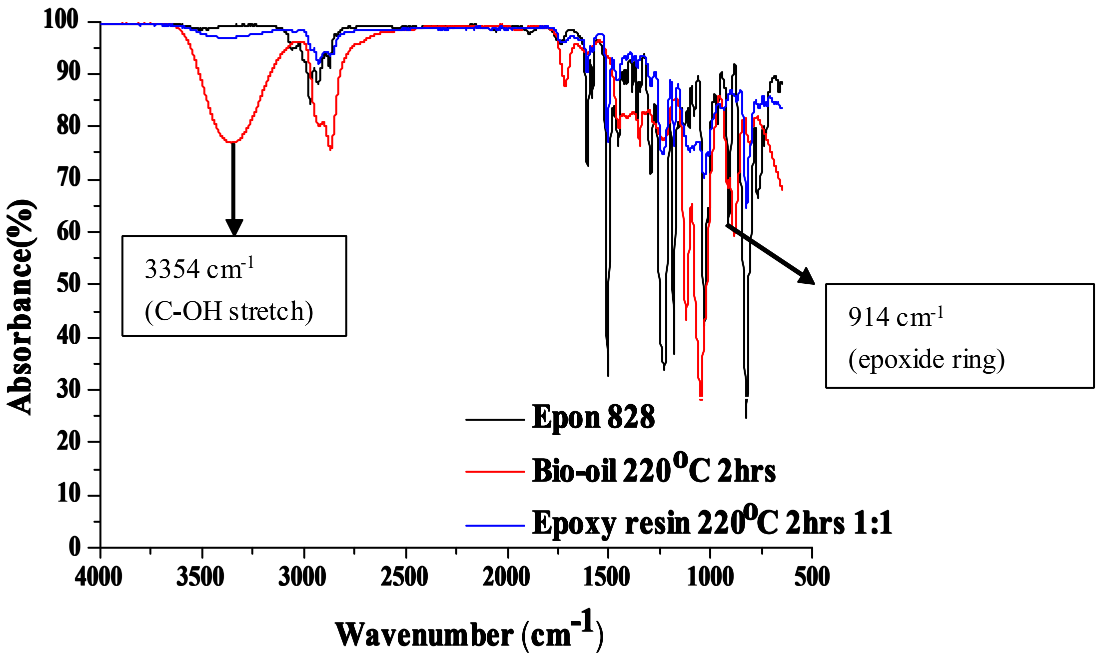


Figure 3.18 FT-IR graph of Absorbance versus Wavenumber for Epon 828, Bio-oil (Liquefaction time was 2h, temperature was 220°C) and bio-oil based epoxy resin.

From the Figure 3.19, when the liquefaction temperature was 220°C and liquefaction time was 2h, the mass ratio of Epon 828 to bio-oil southern pine wood was 1:1. This indicates that biobased epoxy should be manufactured at a 1:1 ratio. In other words, the 1:1 ratio exhibited the highest OH consumption which supported a highly crosslinked structure.

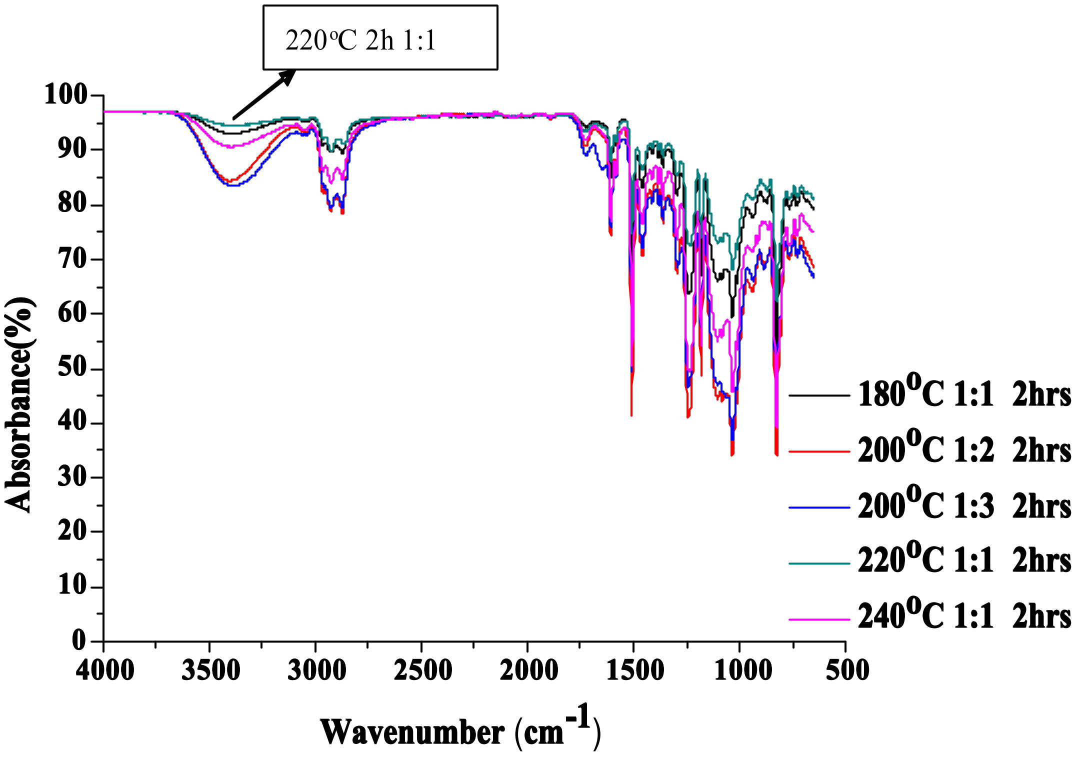


Fig. 3.19 FT-IR graph of Absorbance versus Wavenumber for southern pine wood based epoxy resins when liquefaction time was fixed at 2 h and liquefaction temperature was changed from 180°C to 240°C.

From Figure 3.20, when the liquefaction temperature was 220°C and liquefaction time was 2h, the mass ratio of Epon 828 to southern pine wood based epoxy resin of 1:1 had the lowest OH group which indicates that it had the highest cross linking structure.

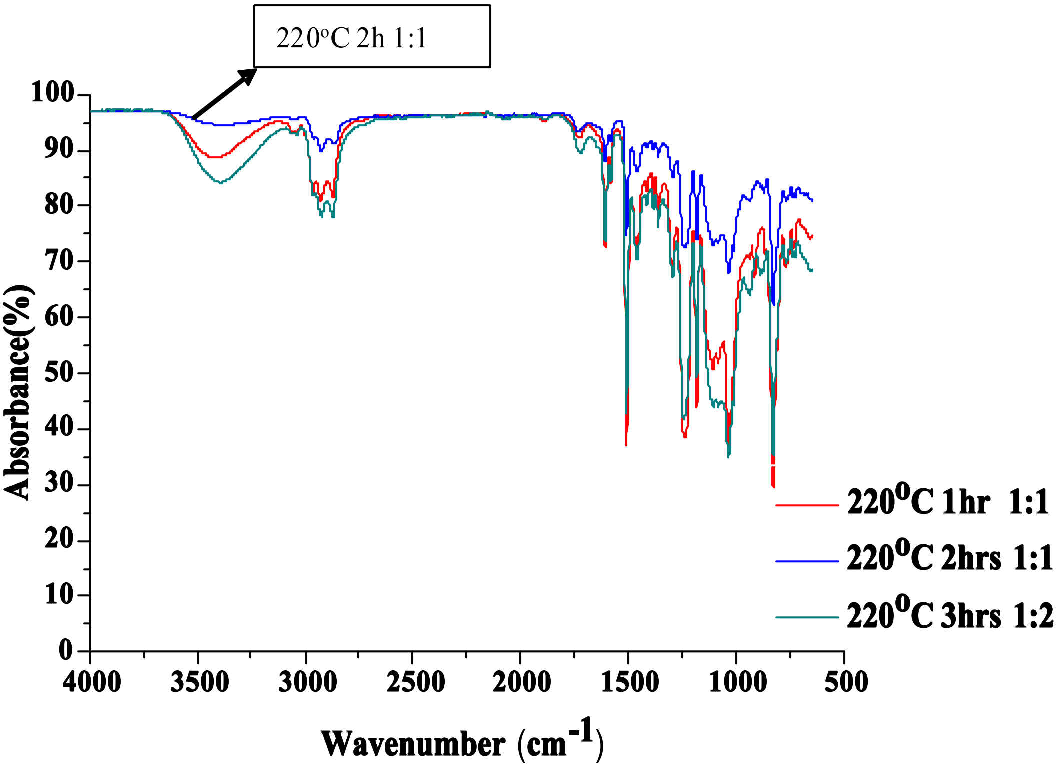


Fig. 3.20 FT-IR graph of Absorbance versus Wavenumber for southern pine wood based epoxy resins when liquefaction temperature was fixed at 220°C and liquefaction time was changed from 1 h to 3 h.

3.4 Conclusions

The following are experimental results (Table 3.5 and Table 3.6) for the whole experiment.

Table 3.5 Experimental Result I

Ratio(Epon:bio-oil)\Temp		180℃	200℃	220℃	240℃
Residue Percentage (%)		61.2	54.3	21.6	28.1
Hydroxyl number (KOH/g)		1078.72±23.33	892.52±2.14	750.60±7.36	790.10±7.10
pH value		2.09	3.07	2.46	2.38
1:1	Tg (℃)	52.44	-	59.73	55.06
	Weight loss (%)	23.10±0.26	-	18.65±0.42	37.82±0.76
	Decomposition temp (℃)	444.31	-	449.77	449.77
1:2	Tg (℃)	-	40.84	-	-
	Weight loss (%)	-	45.93 ±0.83	-	-
	Decomposition temp (℃)	-	446.19	434.53	-
1:3	Tg (℃)	-	30.91	-	-
	Weight loss (%)	-	-	-	-
	Decomposition temp (℃)	-	426.46	-	-
1:4	Tg (℃)	-	-	-	-
	Weight loss (%)	-	-	-	-
	Decomposition temp (℃)	-			

The conditions above are based on the reaction time which is 2 h.

Table 3.6 Experimental Result II

Ratio(Epon:bio-oil)		1h	2h	3h
Residue Percentage (%)		52.78	21.6	46.3
Hydroxyl number (KOH/g)		831.59±1.64	750.60±7.36	848.80±4.67
pH value		2.98	2.46	2.27
1:1	Tg (℃)	57.18	59.73	-
	Weight loss (%)	72.33 ±0.43	18.65±0.42	-
	Decomposition temp (℃)	447.08	-	-
1:2	Tg (℃)	-	-	38.52
	Weight loss (%)	-	-	41.09 ±0.50
	Decomposition temp (℃)	-	-	443.78
1:3	Tg (℃)	-	-	-
	Weight loss (%)	-	-	-
	Decomposition temp (℃)	-	-	-
1:4	Tg (℃)	-	-	-
	Weight loss (%)	-	-	-
	Decomposition temp (℃)	-	-	-

The conditions above are based on the reaction temperature which is 220°C.

"-" means the status of the test samples were too rubbery to be tested.

The liquefaction of southern pine wood produced wood based bio-oil which was utilized to manufacture a new type of epoxy resin. The southern pine wood based bio-oil was successfully reacted with the Epon 828 using TPP as catalyst.

The optimal liquefaction temperature and time was 220°C and 2h, respectively. The optimal mass ratio of Epon to southern pine wood based bio-oil was 1:1, which had the highest crosslinking density.

3.5 Reference

Abdul Khalil, H. P. S., M. M. Marliana, et al. (2011). "Exploring isolated lignin material from oil palm biomass waste in green composites." Materials & Design **32**(5): 2604-2610.

Adler, E. (1977). "Lignin chemistry—past, present and future." Wood Science and Technology **11**(3): 169-218.

Auad, M. L., L. Zhao, et al. (2007). "Flammability properties and mechanical performance of epoxy modified phenolic foams." Journal of Applied Polymer Science 104(3): 1399-1407.

Jasiukaitytė, E., M. Kunaver, et al. (2010). "Lignin behaviour during wood liquefaction—Characterization by quantitative 31P, 13C NMR and size-exclusion chromatography." Catalysis Today **156**(1–2): 23-30.

Jasiukaitytė, E., M. Kunaver, et al. (2009). "Cellulose liquefaction in acidified ethylene glycol." Cellulose **16**(3): 393-405.

Kimura, H., A. Matsumoto, et al. (1998). "Epoxy resin cured by bisphenol A based benzoxazine." Journal of Applied Polymer Science **68**(12): 1903-1910.

Kishi, H., A. Fujita, et al. (2006). "Synthesis of wood-based epoxy resins and their mechanical and adhesive properties." Journal of Applied Polymer Science **102**(3): 2285-2292.

Kobayashi, M., T. Asano, et al. (2004). "Analysis on residue formation during wood liquefaction with polyhydric alcohol." Journal of Wood Science **50**(5): 407-414.

Kunaver, M., S. Medved, et al. (2010). "Application of liquefied wood as a new particle board adhesive system." Bioresource Technology **101**(4): 1361-1368.

Kurimoto, Y., S. Doi, et al. (1999). Species Effects on Wood-Liquefaction in Polyhydric Alcohols. Holzforschung. **53:** 617.

Nonaka, Y., B. Tomita, et al. (1997). "Synthesis of lignin/epoxy resins in aqueous systems and their properties." Holzforschung **51**(2): 183-187.

Pan, H., T. F. Shupe, et al. (2007). "Characterization of liquefied wood residues from different liquefaction conditions." Journal of Applied Polymer Science **105**(6): 3740-3746.

Pan, H., T. F. Shupe, et al. (2008). "Synthesis and cure kinetics of liquefied wood/phenol/formaldehyde resins." Journal of Applied Polymer Science **108**(3): 1837-1844.

Rezzoug, S.-A. and R. Capart (2002). "Liquefaction of wood in two successive steps: solvolysis in ethylene-glycol and catalytic hydrotreatment." Applied Energy **72**(3–4): 631-644.

Tan, T. T. M. (1996). "Cardanol-lignin-based epoxy resins: Synthesis and characterization." Journal of Polymer Materials **13**(3): 195-199.

Vanholme, R., B. Demedts, et al. (2010). "Lignin Biosynthesis and Structure." Plant Physiology **153**(3): 895-905.

Xie, T. and F. G. Chen (2005). "Fast liquefaction of bagasse in ethylene carbonate and preparation of epoxy resin from the liquefied product." Journal of Applied Polymer Science **98**(5): 1961-1968.

Yamada, T. and H. Ono (2001). "Characterization of the products resulting from ethylene glycol liquefaction of cellulose." Journal of Wood Science **47**(6): 458-464.

Yao, Y., M. Yoshioka, et al. (1996). "Water-absorbing polyurethane foams from liquefied starch." Journal of Applied Polymer Science **60**(11): 1939-1949.

Zhao, B. Y., G. Chen, et al. (2001). "Synthesis of lignin base epoxy resin and its characterization." Journal of Materials Science Letters **20**(9): 859-862.

Chapter 4

Modification and characterization of liquefied switchgrass-based epoxy resin

4.1 Introduction

The increased demands for energy along with concerns about energy security and climate change have attracted attention to alternative and renewable energy (Kumar and Gupta, 2009). Among various available renewable energy options, biomass is the only renewable energy source which has the capability of producing petroleum compatible products. Climate change is also one of the most serious environmental concerns. Concentrations of carbon dioxide in the atmosphere will continue rising unless there are major changes made in the way that fossil fuels are used to provide energy. Globally, biomass feedstock will be a primary source of energy during the next century. It is recommended that modern bioenergy systems be an important contributor in future sustainable energy systems and sustainable development of industrialized and developing countries (Berndes, Hoogwijk et al., 2003). Biomass is a biological material, which includes both animals and plants. Biomass resources include wood and wood waste, animal manure, agricultural crops and crop waste, aquatic plants, and energy crops. Milling activities create huge quantities of mixed biomass such as wood, cooking wastes, sewage sludge, and manure. Plant biomass is typically composed of lignin, cellulose, hemicelluloses and various other minor compositions depending on plant species. Cellulose and lignin are two most abundant biopolymers in plant materials, both of which sequester carbon during tissue development. Lignin is an amorphous phenolic polymer, which consists of p-hydroxyphenylpropane, guaiacylpropane, and syringylpropane monomers. Cellulose is a linear polymer of glucopyranose with molecular weights more than 100,000. Mannose, xylose, and glucose polymerize to form hemicelluloses.

In the liquefaction of biomass, using a solvent reagent and an acid catalyst has been studied as a novel technique to utilize biomass as an alternative to petroleum-based products during chemicals production. Likewise, phenol is one of the most commonly used reagent solvents for wood liquefaction. Wood liquefaction with phenol can be developed into novolac or resol type phenolic resins. A variety of general studies have been carried out on wood liquefaction with phenol, but recently its use has been questioned because it comes from a petroleum based process and can be dangerous to human exposure. In this research, the principal material to generate bio oil through liquefaction is switchgrass. It is a perennial warm season bunchgrass native to North America, where it occurs naturally from 55°N latitude in Canada southwards into the United States and Mexico. Switchgrass is one of the dominant species of the central North American tall grass prairie and can be found in remnant prairies, in native grass pastures, and naturalized along roadsides. The average composition and the standard deviation of the chemical ratios are listed in Table 4.1 results expressed as %w/w of dry lignocellulose (Mei Zhen, Da Chun et al., 2010).

Table 4.1

The average composition and the standard deviation of the determination of six different samples (Mei Zhen, Da Chun et al., 2010)

Fraction	Average	Std dev
Ash	6.8	0.08
Hot water Extractives(100℃)	5.5	0.07
Klason lignin	18.7	0.43
Glucan	40.6	0.38
Xylan	22.8	0.55
Glacan	3.6	0.03
Others	2.4	0.04
Mass balance	100.4	0.12

For the last ½ decade, epoxy resins have been commercialized for major industrial applications such as adhesives, coatings, moldings, and so on (Wu and Lee, 2010). Use is especially important where technical superiority warrants their higher costs when compared to other thermosets. In study of Liu et al. (1997), the low shrinkage on cure, characteristics of toughness, high adhesion to many substrates, moisture resistance, good alkali, and versatility in formulation make epoxy resins widely used in adhesive, laminating, coating, and casting applications (Liu, Hsiue et al., 1997). In this research, epoxy resin was mixed with liquefied bio-oil from switchgrass feedstock. The final mixture of these two chemical substances with an optimal ratio formed a new bio-based type adhesive. There are many studies about the properties of conventional epoxy resin. In the research of Justin D. Littell et al. (2008), the epoxy specimens were tested in tension, compression, and tensional loadings under various strain rates ranging from 10^{-5} to $10^{-1}s^{-1}$ and temperatures ranging from room temperature to 80°C(Littell, Ruggeri et al., 2008). To test the specimens at high temperatures, a specialized clear temperature chamber was used. They found that the test procedure developed could accurately and quickly categorize the material response characteristics of an epoxy resin. In addition, the results displayed clear strain rate and temperature dependencies in the material response to loading. In another study, they used destructive and non-destructive tests to test the mechanical properties of epoxy resins and random fiber epoxy systems (Prassianakis, Kytopoulos et al., 2006). In the research of H.P.S Abdul Khalil et al. (2011), they generated the use of EFB-lignin as curing agent in epoxy resin (Abdul Khalil, Marliana et al., 2011). Based on their theory, the deduction of this research is shown in reaction Figure 4.1.

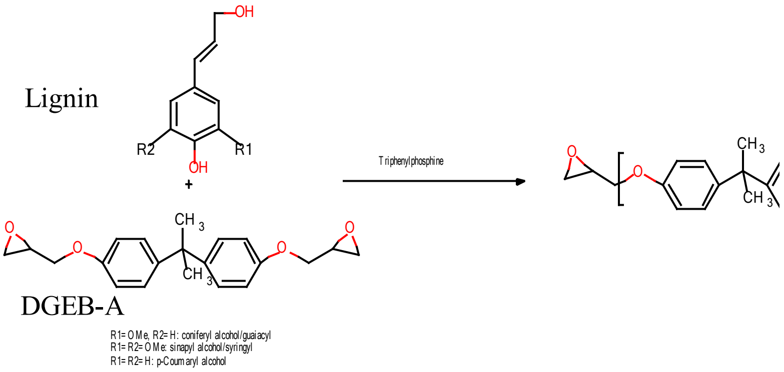


Fig. 4.1 Idealized network formation during curing reaction of epoxy-lignin system.

In the study of Maria L. Auad et al. (2007), they mainly focused on the development and optimization of the processing methodology to produce epoxy modified phenolic foams, and they analyzed the relation between the composition and the structure as well as the mechanical and flammability performance of epoxy-phenolic (E-P)-based foams, as shown in reaction scheme in Figure 4.2 (Maria L. Auad, Zhao et al., 2007). The epoxy they used was Epon 826 and the hydroxyl group supplier was Novolac, which were Epon 828 and southern pine wood based bio-oil. They have similar reaction theory to produce epoxy resin.

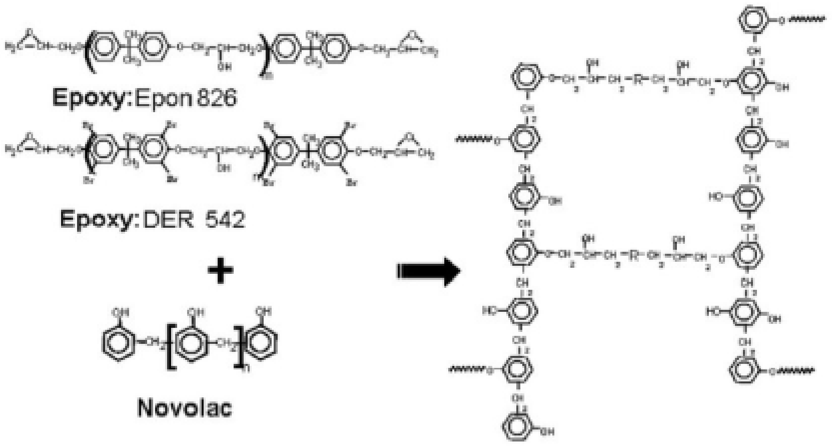


Fig.4.2 Schematic of the E-P systhesis reaction (Maria L. Auad, Zhao et al., 2007)

4.2 Materials and Methods

The following is flow chart (Figure 4.3) of this experiment that show to optimize the liquefaction temperature when the liquefaction time was fixed at 2h in the research project. The flow chart is similar with Chapter 3 Figure 3.4 and Figure 3.5 except changing raw material from southern pine wood to switchgrass and the liquefaction temperatures are 200°C, 220°C, 240°C, 250°C and 260°C.

Fig. 4.3 Flow chart of optimizing the liquefaction temperature when the liquefaction time was fixed at 2h.

Prior to this study, preliminary studies were carried forth to determine the basic parameters necessary for liquefaction and epoxy polymer synthesis. It was found that 250℃ was the best liquefaction temperature while 2 h appeared to be sufficient to yield good bio-oil visually. We then developed an experimental design around the base temperature by varying the time to 1, 2 and 3h. The response variables for this experimental design included: liquefaction residue, hydroxyl number test, pH value of bio-oil, and the thermal properties tests of switchgrass based epoxy resin.

4.2.1. Biomass (switchgrass) Preparation

A hammer mill (New Holland grinder model 358, New Holland, PA.) with 3.175-mm (1/8 in.) sieve size was used for particle size reduction. Particles from the switchgrass (Panicum virgatum) was collected and oven-dried at 105℃ for 12hrs and kept in a desiccator at room temperature before use. The dried material was ground to pass through a 20 mesh sieve before put into oven. Diethylene glycol (99%, from Alfa Aesar chemical company) was used as the reagent solvent in the liquefaction. All other main chemicals for liquefaction of switchgrass and synthesis of wood-based epoxy resins include triphenylphosphate, 98% sulfuric, phthalic anhydride and pyridine. They were all reagent grade, and used without further purification.

4.2.2 Liquefaction of switchgrass

The liquefaction procedure of switchgrass was based on the general method described by Tao Xie(Xie and Chen, 2005),and then subsequently modified by Matjaž Kunaver (Kunaver, Medved et al., 2010).The liquefaction of switchgrass was carried out in a 1000 ml three neck glass reactor equipped with a mechanical stirrer (500 rpm) and reflux condenser device. The reactor was charged with 100g of wood and 400g of diethylene glycol when the flask was heated to the desired temperature for liquefaction. 1 g of 98% sulfuric acid was added. The mixture was heated for various times (1h, 2h and 3h) and at various temperatures (180℃, 200℃, 220℃ and 240℃) while being constantly stirred.

4.2.2.1 Determination of residue content

The residue content evaluation method used in this work was same with Chapter 3 but changed determination object from southern pine wood liquefaction residue to switchgrass liquefaction residue. Specific equation refers to Chapter 3 equation (1).

4.2.2.2 Hydroxyl group number test

The hydroxyl number was measured according to ASTM D4274-11, which was same with Chapter 3 however changed detection objects from southern pine wood based bio oil to switchgrass based bio oil.

4.2.2.3 PH value examination

Fisher Scientific AR 20 pH/Conductivity Meter was employed for determining the Ph value of various switchgrass based bio-oil.

4.2.2.4 FT-IR characterization of bio-oil and biobased epoxy reactions

The Fourier Transform Infrared (FT-IR) analysis of the liquefied switchgrass residues was performed by an FT-IR spectrometer (PerkinElmer, model Spectrum 400), which was same method and device with Chapter 3 but changed examine object from southern pine wood based bio oil to switchgrass based bio oil.

4.2.3 Preparation of switchgrass-based epoxy resin

The method of preparation of swichgrass based epoxy resin refers to the method used in Chapter 3 except using switchgrass based bio oil as reactants.

4.2.4 Analytical methods

Analytical methods used in this work were same as Chapter 3 which were used to character the liquefied biomass based epoxy resin, but the southern pine wood based epoxy resin was changed to switchgrass based epoxy resin.

4.2.5 Data Analysis

All analysis of data sets and plotting of graphs were performed using Origin 8.0 software (Version 8.0, OriginLab Corporation, Microcal Software).

4.3 Results and Discussion

4.3.1 Residue content of liquefied switchgrass

Figure 4.5 (a) and (b) show the residue content of liquefied switchgrass processed at different time and temperatures. With increasing temperature, the residue decreased in a linear fashion. This was different than wood which saw a leveling off of residue after 220°C. Figure 4.4 (a) and (b) indicate that the longer liquefaction time was not better because when the liquefaction time was 2 hours the lowest residue content was observed. The residue content of liquefied switchgrass and southern pine wood had similar results which proved the general tendency in the analysis of liquefaction residues.

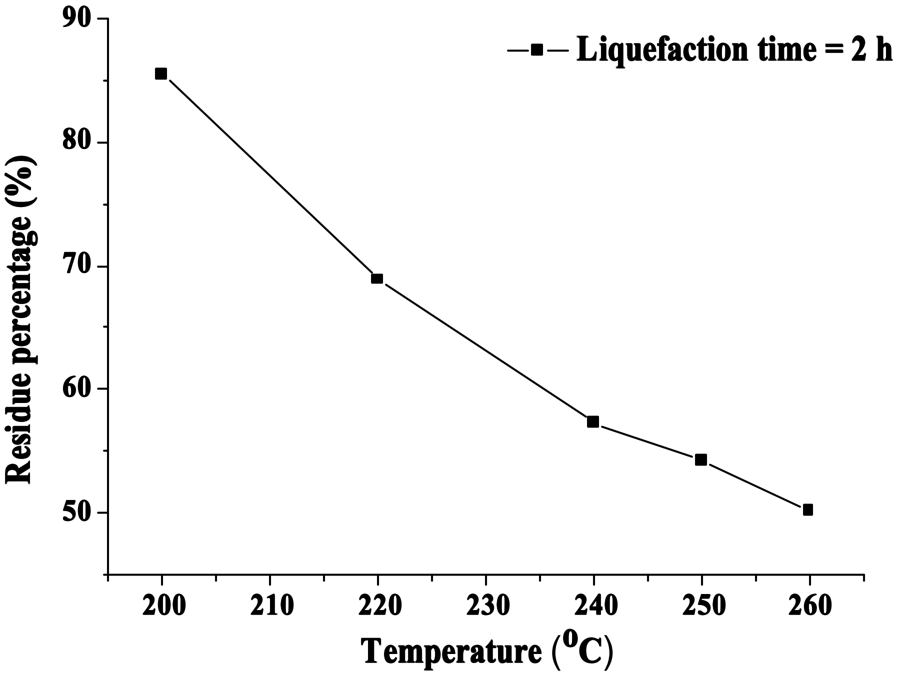


Fig. 4.4 (a) Relationship between the liquefaction temperature and residue percentage

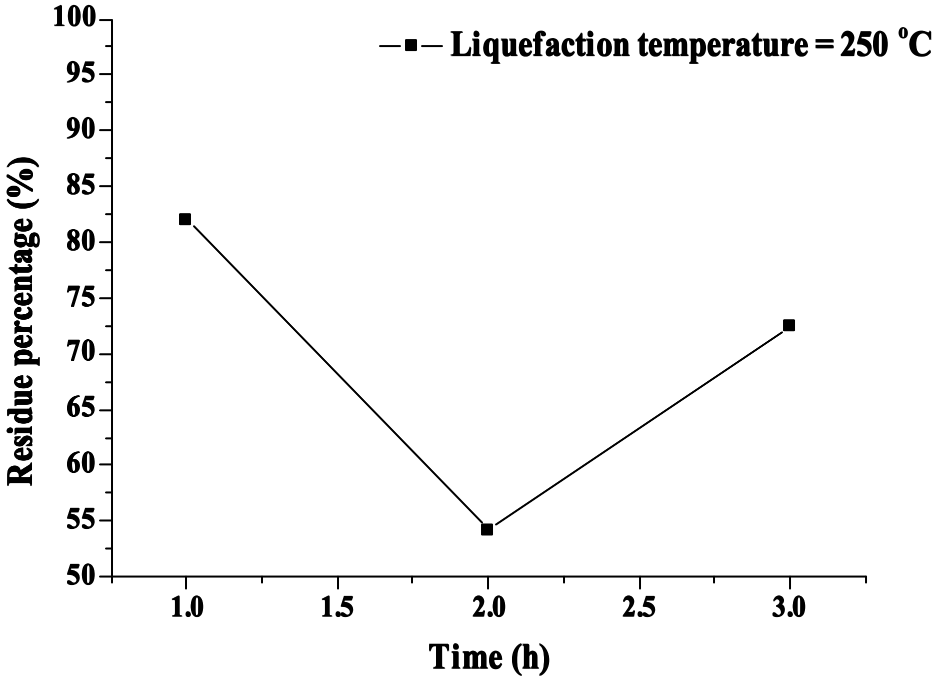


Fig. 4.5 (b) Relationship between the liquefaction time and residue percentage.

4.3.2 Hydroxyl number and pH value of liquefied switchgrass

During the synthesis of epoxy phenolic resins, there is assumed to be a reaction between the OH groups of the novolac phenolic resin to the epoxy:epon structure (Auad et al. 2006). This reaction mechanism forms a 3 dimensional crosslinked structure and the density of that structure should depend on the molar ratio of phenolic supplied OH groups to epoxy groups. For this study, the bio-oil from liquefaction is more complex than simply measuring the amount of phenolic groups. It is instead probably similar to pyrolysis oil in which many compounds are present other than phenols and thus OH separation and quantification may be difficult (Thangalazhy-Gopakumar et al. 2010). Characterization of the origin of the OH groups can be challenging although Ben and Ragauskas (2011) have recently developed a pNMR technique that partitions out the hydroxyl group amount for aliphatic OH, phenolic OH, guaiacyl phenolic OH, catechol type OH, p-hydroxy-phenyl OH, and acid OH. But pNMR is a complex technique and not always widely available and thus for this study, the total OH number was measured through titration methods.

The total hydroxyl number decreased steadily till 250°C and then rises sharply at 260 °C in Figure 4.5 (a). The decrease in hydroxyl group at temperatures below 250°C agreed with Wang and Chen (2007) who pursued the rapid liquefaction of wheat straw. In that study, at lower temperatures there was a steeper drop in OH number than at higher temperatures. However, our study operated at higher temperatures than that study and the hydroxyl group number reversed direction at 260°C in Figure 4.5(b). Similar increases in hydroxyl groups, using the absorbance in the infrared region as an indicator, were observed at 280 °C when hot compressed water was used to liquefy paulownia (Sun et al. 2011). They attributed this increase in OH to condensation reactions. Perhaps that same rational can be assumed for Fig. 2b in which the OH number increased dramatically from 2 to 3 hours. This suggests that the severity treatment can be used to manipulate the OH number during liquefaction.

It was also observed that the overall bio-oil OH number was higher than many other studies. Zheng et al. (2011) used phenol based solvents and found hydroxyl groups between 280 and 622 mg KOH/g and this was dependent on the whether the heating source was microwave or heat bath. Pan et al. (2012) suggest that the solvent and/or catalyst play an important role in OH number. In that study, when sulfuric acid was used, numbers similar to other studies were observed (Zheng et al. 2011) but when phosphoric acid was used, OH numbers as high as 700 mg KOH/g can be reached (Pan et al. 2012). For our study, a 1:4 wood to diethylene glycol ratio was used to liquefy the switchgrass. The high level of diethylene glycol may help to explain the higher OH numbers of the liquefaction oil. For example, Nasar et al. (2010) found that as the amount of ethylene glycol amount increased, the hydroxyl number in the liquefaction oil increased. This suggests that diethylene glycol not only acts as a solvent but supplements the overall contribution in OH number for the liquefied biomass. This may be an important benefit if the manufacturer would like to control the overall OH group number by controlling the solvent volume during liquefaction. In the research of Yao et al. (1996), when the glycols were subjected to the same liquefaction conditions, it was found that the OH groups plateaued with temperature. This indicated that the main decrease in OH number in the reaction mixture was due to the reaction between the main wood components and the glycols that were present.

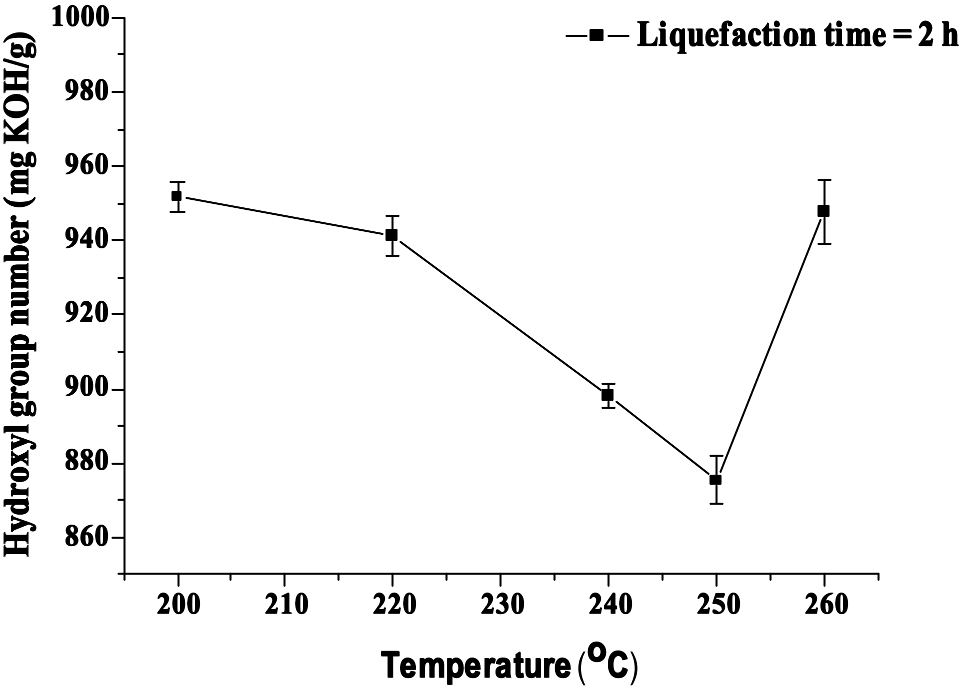


Fig. 4.5 (a) Relationship between the liquefaction temperature and the hydroxyl group number.

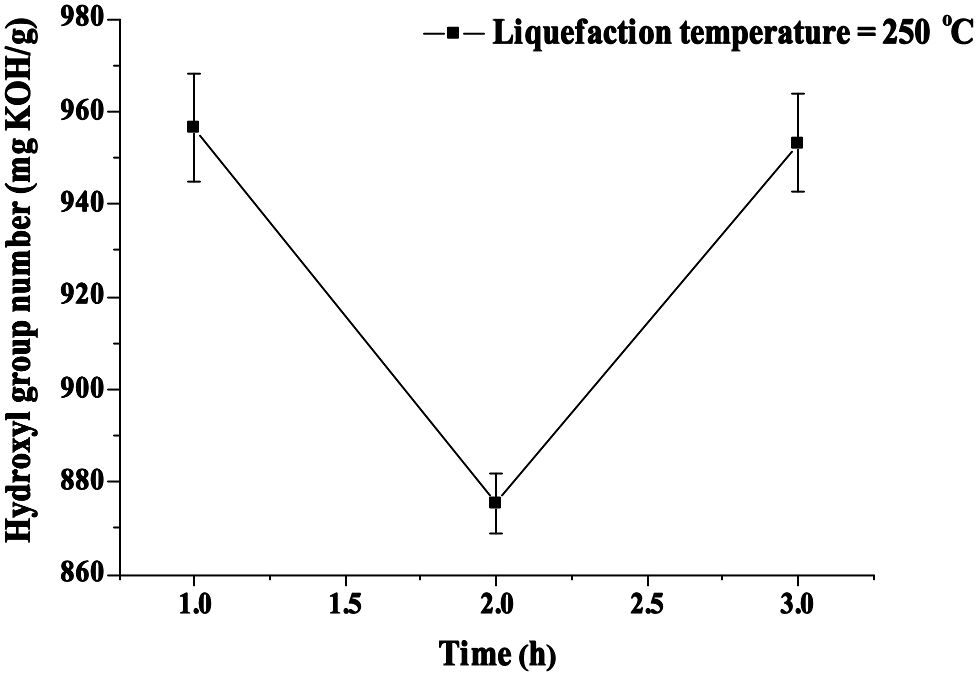


Fig. 4.5 (b) Relationship between the liquefaction time and hydroxyl group number.

As the liquefaction temperature was increased from 200°C to 260°C, the pH value tended to increase. Additionally the highest pH value was observed at 250°C. When the liquefaction time was changed from 1h to 3 h, the 2 h run had the lowest pH value which was similar to wood in chapter 3.

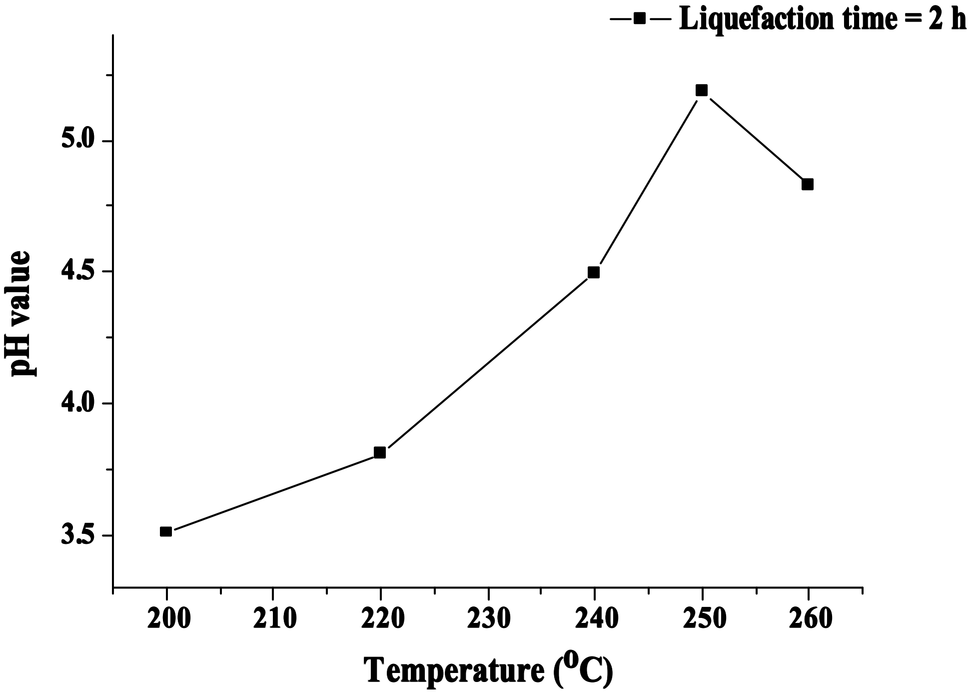


Fig. 4.6 (a) Relationship between the liquefaction temperature and pH value.

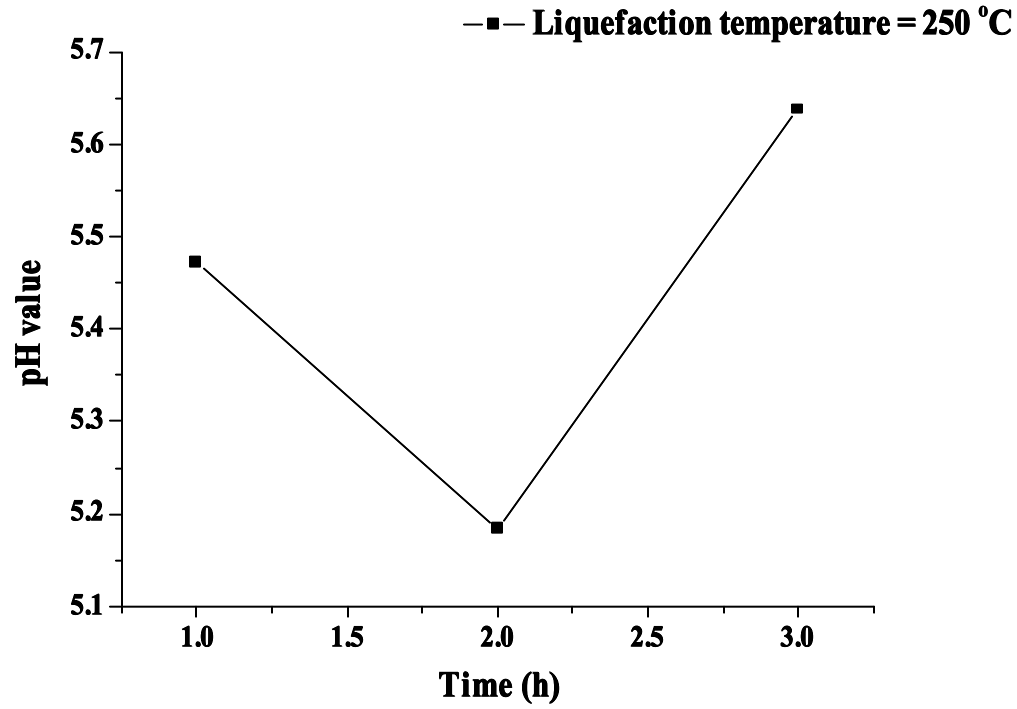


Fig. 4.6 (b) Relationship between the liquefaction time and pH value.

4.3.3 Differential Scanning Calorimeter (DSC)

The DSC was used to assess the glass transition temperature of the bio-based epoxy resin. The liquefaction conditions and ratios (Epon 828: bio-oil) were investigated as experimental factors for DSC analysis. From Figure 4.7 and Figure 4.8, it can be observed that the thermograms consist of one endothermic peak which ranged from 30°C to 65°C in various samples. Table 4.2 shows the specific glass transition temperature for each sample. The different modification conditions showed endothermic cure peaks similar to each other. The sample with 250°C as a liquefaction temperature and a 1:1 ratio had the highest glass transition temperature. This was probably an indication that the crosslinking density was highest at this ratio. Thus, the ratio 1:1 (Epon 828: swithcgrass based bio-oil) was the optimal ratio for the epoxy resin productions. The liquefaction temperature at 250°C was optimal temperature for liquefaction.

The Tg of 64°C was 20°C lower than a similar study that utilized polyethylene glycol, glycerol, and sulfuric acid for liquefaction of wood (Wu and Lee 2011). That study exhibited a similar decrease in Tg with the addition of liquefaction oil which was an indication of decreased crosslinking. The Tg observed in this study was lower than other bio-oil based epoxy systems (Xie and Chen 2005) and even lower than the Tg of a similar feedstock (lignin) which normally exhibits a Tg range of 150 to 165°C (Mansouri et al. 2011). The lower Tg observed in this study may be attributable to the large volume of diethylene glycol solvent which acted as a plasticizer and lowered the Tg of the composite matrix (Lourdin et al. 1997). Vanin et al. (2005) found diethylene glycol to provide the largest plasticizer effect resulting in the lowest Tg in films when compared to other common plasticizers such as glycerol, propylene glycol, and ethylene glycol. Plasticizers generally function to modify the interchain interactions resulting in a rubbery response due to enhanced flexibility. The low Tg in this study may thus be attributable to the plasticizing influence of diethylene glycol which apparently is retained after liquefaction as further evidenced by the high OH number within the bio-oil feedstock in Figure 4.5. To our knowledge, there are no other studies that have found this effect on Tg for epoxy-bio-oil based polymers.

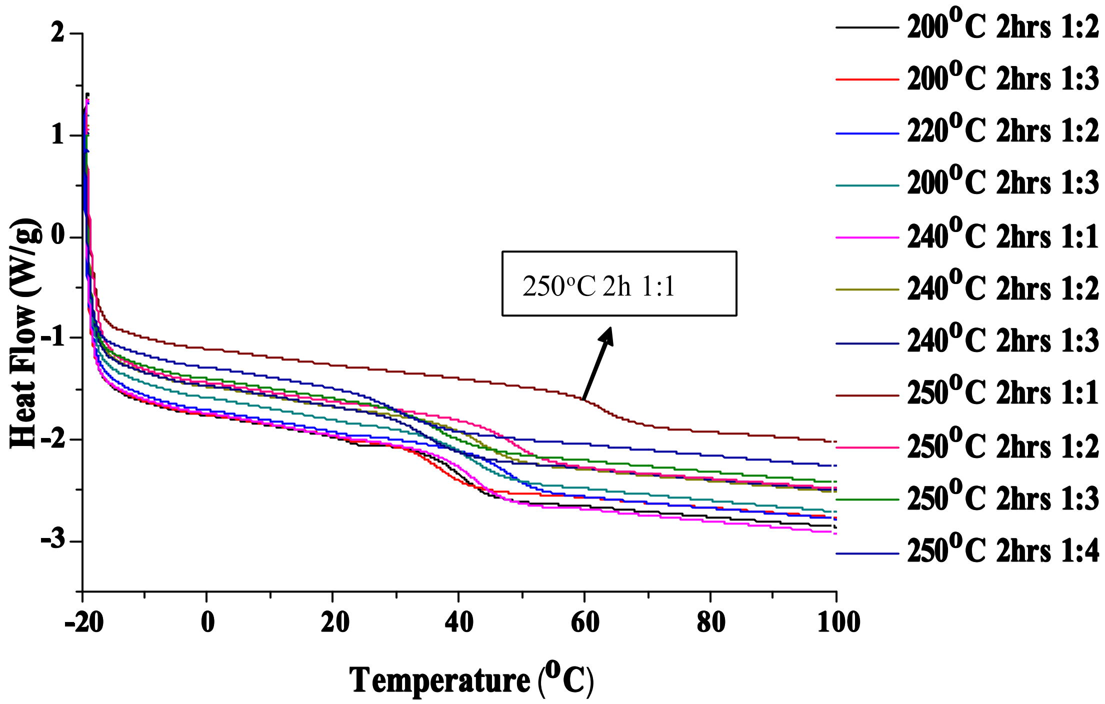


Fig. 4.7 DSC results of different samples at different liquefaction temperatures and ratios of Epon 828 to switchgrass based bio-oil.

Table 4.2 Specific DSC results of different samples at different liquefaction temperatures and ratios of Epon 828 to switchgrass based bio-oil.

“-” means the status of the test samples were too rubbery to be tested.

Temperature (℃)	Ratio of Epon 828 to Bio-oil			
	1:1	1:2	1:3	1:4
200	-	40.47	37.15	-
220	38.44	48.76	42.41	-
240	42.93	42.68	35.65	-
250	62.84	48.69	35.86	28.25

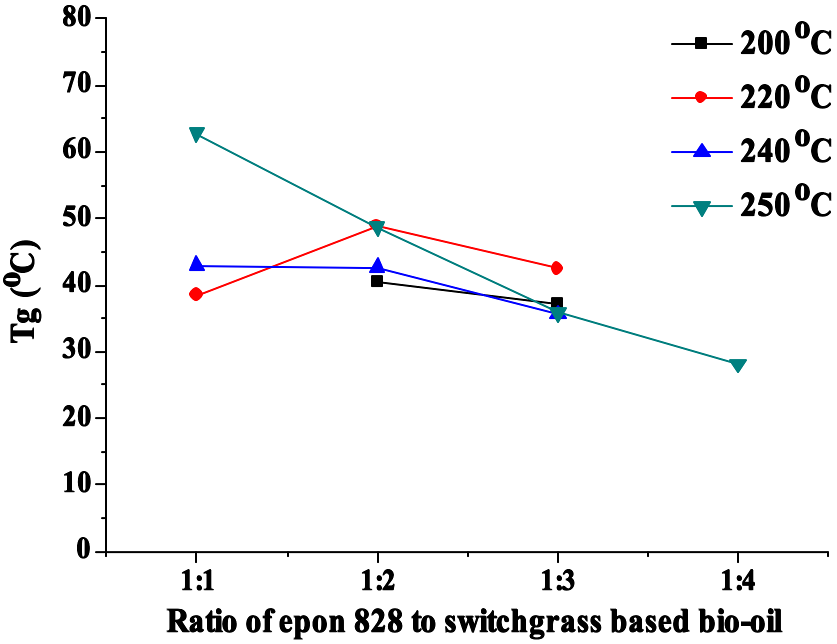


Figure 4.8 Specific DSC results of different samples in different liquefaction temperatures and ratios of Epon 828 to switchgrass based bio-oil.

Figures 4.9 and 4.10 as well as Table 4.3 indicates the optimal liquefaction time was 2 h and the optimal ratio of switchgrass based bio-oil was 1:1 – the ratio which had the highest glass transition temperature 62.8°C. This indicates that the degree of crosslinking for this treatment combination was the highest.

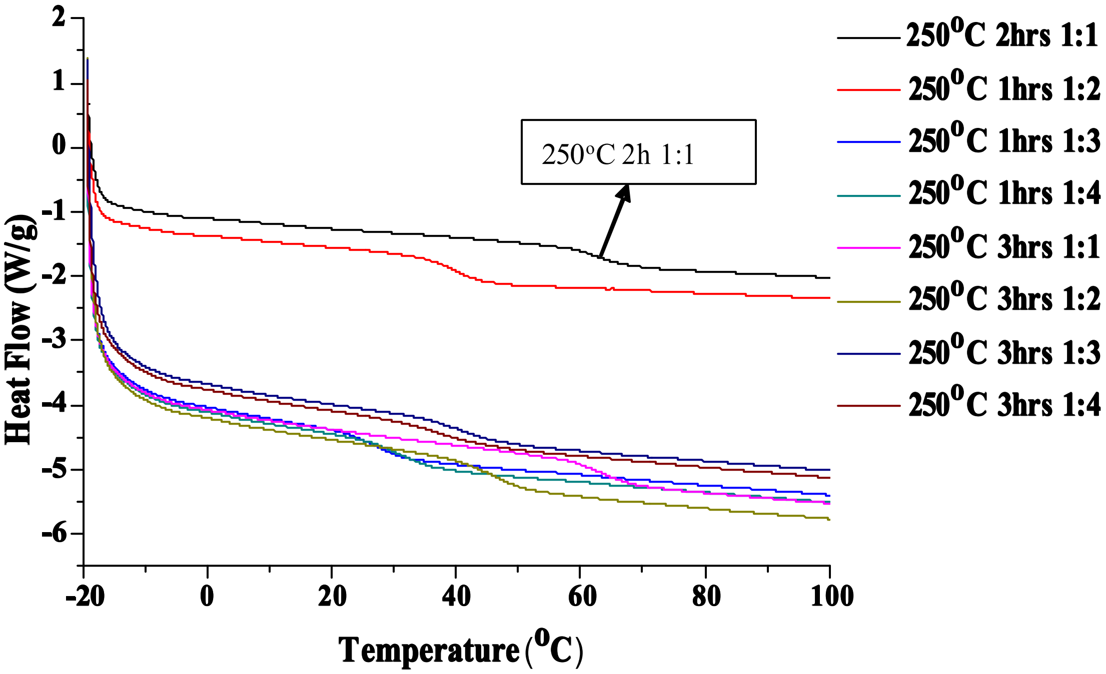


Fig. 4.9 DSC results of different sample at different liquefaction times and ratios of Epon 828 to switchgrass based bio-oil.

Table 4.3 Specific DSC results of different sample at different liquefaction times and ratios of Epon 828 to switchgrass based bio-oil.

"-" means the status of the test samples were too rubbery to be tested.

	Ratio of Epon 828 to Bio-oil			
Time (h)	1:1	1:2	1:3	1:4
1	-	40.16	26.81	31.02
2	62.84	48.69	35.86	28.25
3	62.23	45.64	40.44	35.61

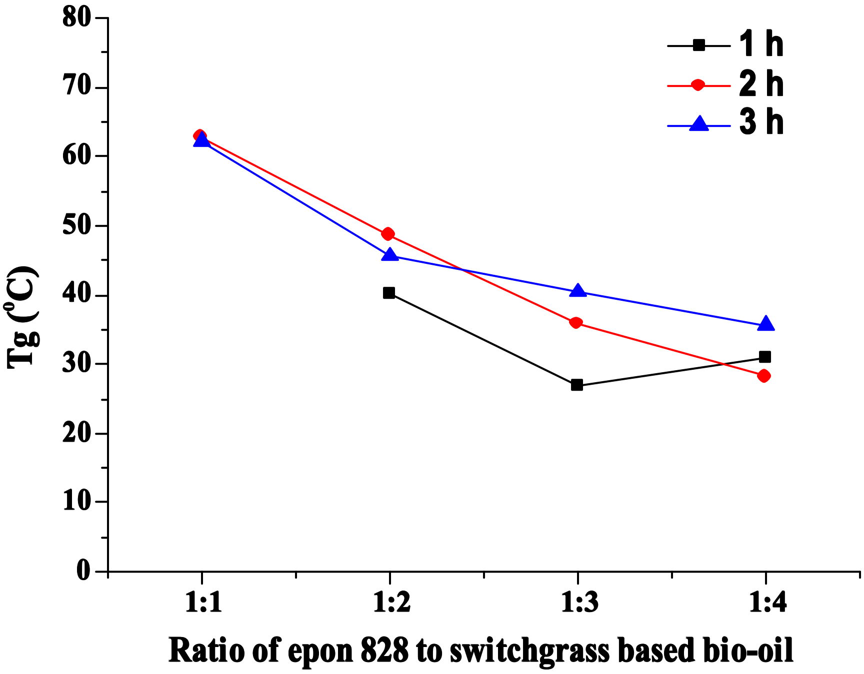


Figure 4.10 Specific DSC results of different sample at different liquefaction times and ratios of Epon 828 to switchgrass based bio-oil.

4.3.4 Thermo Gravimetric Analyzer (TGA)

In the TGA figures, two different decomposition temperatures, 390°C and 550°C, were observed to represent the primary peaks associated with switchgrass based epoxy resin degradation. This is similar to Chen et al. (2008), who observed three overlapping peaks at 245°C, 418°C, and 545°C in the DTG (Derivative Thermogravimetric) curves for a commercial resol PF adhesive. The first temperature peak in this research was 390°C, which was attributed to the stage where methylene bridges decompose or are broken into methyl groups. The degradation of phenols occurs in the second stage, which occurs at 550°C. In the first stage, with 250°C as the liquefaction temperature, 2 h as the liquefaction time, and 1:1 as the mass ratio of Epon 828 to switchgrass based bio-oil, the highest degradation temperature was observed. The second temperature peak in this research was the degradation of phenols which temperature was 530°C, according to literature, and in this research was 550°C. The results obtained from the TGA thermograms in the second degradation stage also showed that when the liquefaction temperature was 250°C, fixed liquefaction time was 2 h, and the mass ratio of Epon 828 to switchgrass based epoxy resin 1:1 had the highest degradation temperature.

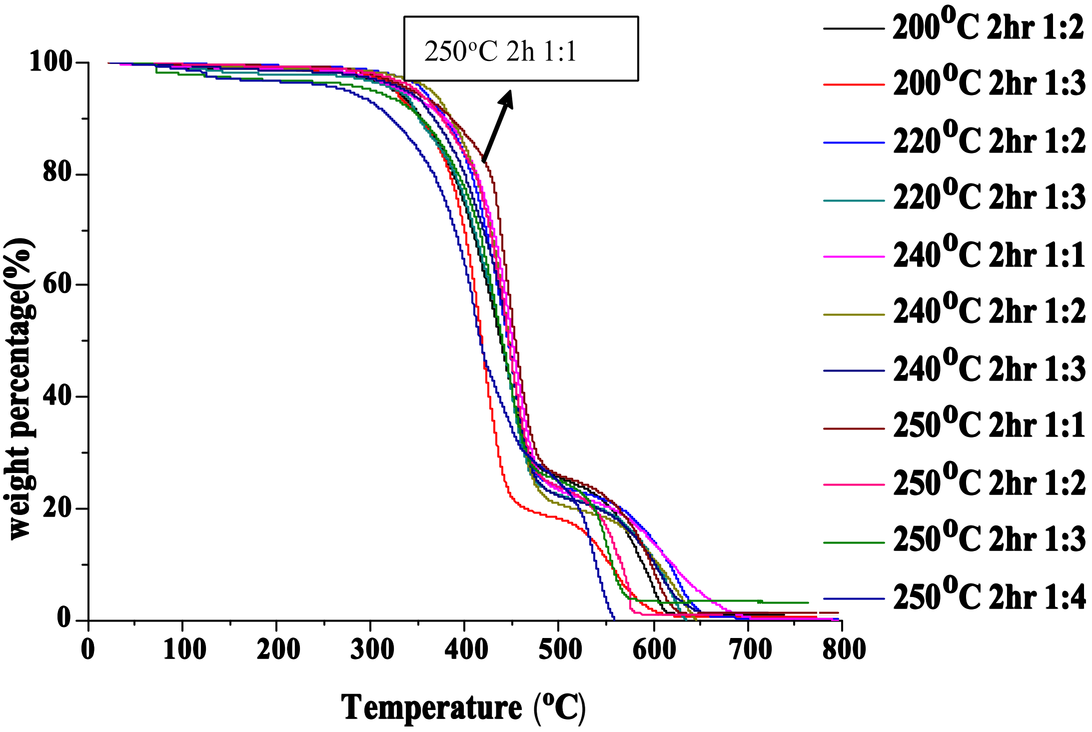


Fig. 4.11 Thermogravimetric (TG) curves for switchgrass based epoxy resins when liquefaction time was fixed at 2 h and liquefaction temperature was changed from 200°C to 260°C.

From Figure 4.12, when the liquefaction temperature was 250°C and the fixed liquefaction time was 2 h, the mass ratio of Epon 828 to switchgrass based epoxy resin of 1:1 had the highest degradation temperature during the first degradation stage.

When the liquefaction temperature was 250°C, the liquefaction time was 3 h, and the mass ratio of Epon 828 to switchgrass based epoxy resin of 1:1 had the highest degradation temperature.

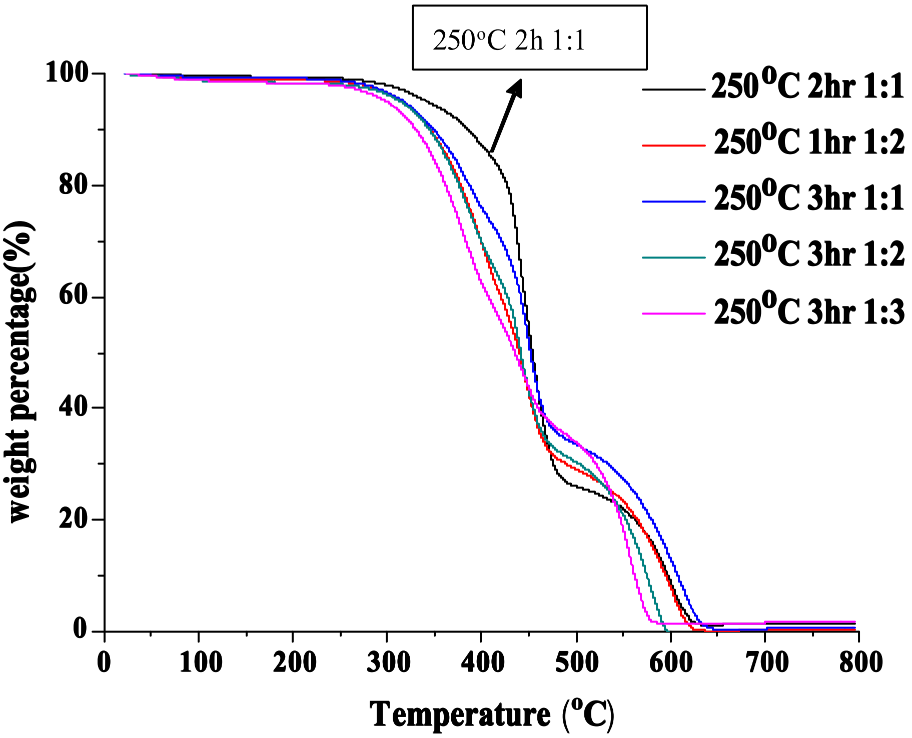


Fig. 4.12 Thermogravimetric (TG) curves for switchgrass based epoxy resins when liquefaction temperature was fixed at 250°C and liquefaction time was changed from 1 hour to 3 h.

4.3.5 DMA results

Figure 4.14 shows the Dynamic viscoelastic properties of the switchgrass based epoxy resins. The cured switchgrass based epoxy resins showed high stiffness at room temperature and rubbery plateau after T_g. The storage modulus of elasticity of the different samples at 25°C was close to each other. Additionally the rubbery plateau indicates that a crosslink network structure was surely formed. The highest T_g occurred in the sample formed when the liquefaction temperature was 250°C, the liquefaction time was 2 h, and mass ratio of Epon 828 to bio-oil was 1:3. However, the orange curve which is when liquefaction temperature was 250°C, the liquefaction time was 2 h, and mass ratio of Epon 828 to bio-oil was 1:1 has the highest value. This indicates that the orange curve sample has the highest percentage of crosslinking.

As can be observed, once the Tg is reached, a rubbery plateau was achieved for most treatments. Liquefaction at 250°C and an epoxy:oil ratio of 1:1 provided the highest storage modulus when the Tg was exceeded. On the other hand, the storage modulus at lower temperatures and/or at 1:2 or 1:3 ratios were superior at temperatures below Tg. This suggests that more flexibility in recipe may be possible for low temperature product applications.

One of the advantages of the current system is that up to 50% of the weight of the polymer consists of bio-oil and this was competitive or better than similar studies. For example, Nonaka et al. (1997) was able to achieve maximum storage modulus when 50% industrial kraft lignin (by weight) was used to synthesize epoxy-lignin resins. They found considerable differences in the E' to temperature trends for different loadings of lignin. Unlike this study, they were able to achieve higher Tg values (around 140°C) for a similar bio-derived substitution rate and the Tg seemed to approach that typical of pure lignin (Mansouri et al. 2011). But for our study, despite bio-oil being similar to lignin in basic composition, the lower Tg may have been attributable to the plasticizing effect of diethylene glycol within the epoxy to oil cross-linked matrix.

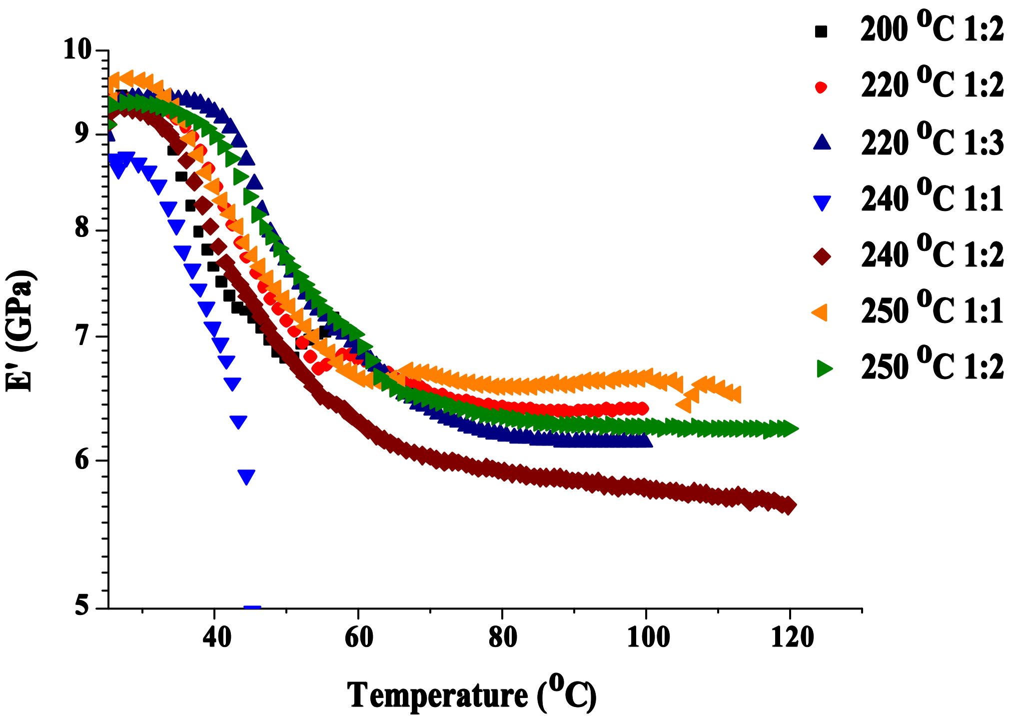


Fig. 4.13 Storage modulus (E') for switchgrass based epoxy resin systems.

4.3.6 Extraction tests

In order to determine the solubility which should be directly related to crosslink density, extraction teste were performed. The more stable epoxy resin was found by analyzing which ratio of Epon 828 to Bio-oil had the higher percentage of crosslinked structure. After 4 hours extraction, the minimum Epon 828: switchgrass bio-oil ratio was 1:4 which was illustrated in Table 4.4 and Figure 4.14

Table 4.4 The Acetone Soxhlet extraction tests of switchgrass based epoxy resin at different liquefaction temperatures.

"-" means the status of the test samples were too rubbery to be tested.

Temperature (℃)	Mass ratio Epon 828 : Bio-oil							
	1:1		1:2		1:3		1:4	
	Avg(%)	SD	Avg(%)	SD	Avg(%)	SD	Avg(%)	SD
200	-	-	61.96	0.43	60.94	0.86	-	-
220	-	-	46.48	0.34	57.30	0.67	62.00	0.41
240	79.59	0.63	65.18	0.58	71.46	0.80	67.70	0.67
250	41.89	0.78	50.64	0.53	67.60	0.40	61.40	0.42

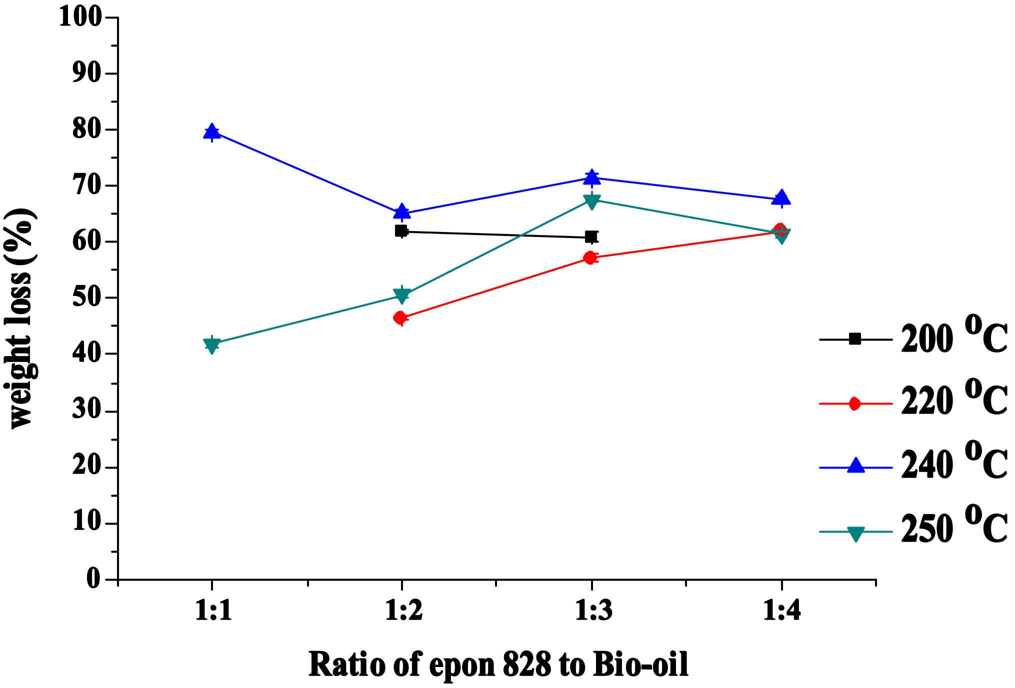


Fig. 4.14 The acetone Soxhlet extraction tests of switchgrass based epoxy resin at different liquefaction temperatures.

The results of the Acetone Soxhlet extraction tests are presented in Table 4.4 and Figure 4.14. The change in mass loss for different ratios and temperatures is illustrated. The lowest response in weight loss was 41.9 and was a result of the epoxy resin formed with a 1:1 ratio and a liquefaction temperature of 250°C. This was much higher than liquefied wood based epoxy resins (Chapter 3) and suggests that wood based epoxy resins exhibit a higher degree of cross linking.

Table 4.5 The Acetone Soxhlet extraction tests of switchgrass based epoxy resin at different liquefaction times.

"-" means the status of the test samples were too rubbery to be tested.

Time (h)	Mass ratio Epon 828 : Bio-oil							
	1:1		1:2		1:3		1:4	
	Avg(%)	SD	Avg(%)	SD	Avg(%)	SD	Avg(%)	SD
1	-	-	59.19	0.69	53.30	0.16	63.47	0.29
2	41.89	0.78	50.64	0.53	67.60	0.40	61.40	0.42
3	54.97	0.61	50.97	0.72	54.46	0.90	54.64	0.36

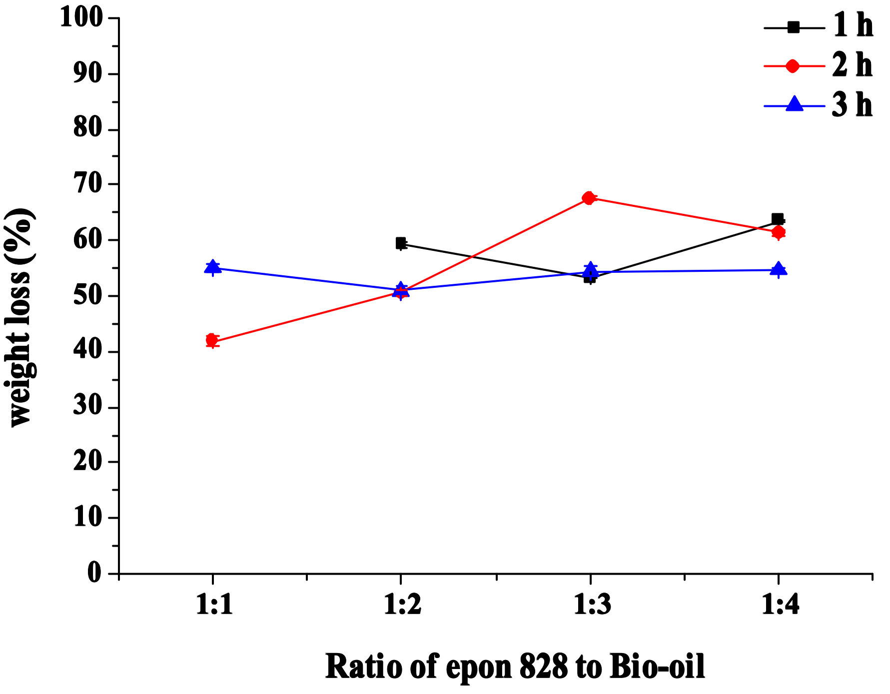


Fig. 4.15 The acetone Soxhlet extraction tests of switchgrass based epoxy resin at different liquefaction times.

From the Table 4.5 and Figure 4.15, it is observed that the lowest mass loss occurred in the same sample where the ratio of Epon 828 to Bio-oil was 1:1 and the liquefaction time was 2h, and the liquefaction temperature was fixed at 250°C.

4.3.7 FT-IR spectroscopy

The composition of the polymeric materials can be determined by measuring the response in infrared spectra with a change in liquefaction conditions or Epon to bio-oil ratio. A FT-IR spectrometer was used and the peaks were compared to commercially available spectral data bases. FT-IR identifies the types of chemical bonds (functional groups) present in the solid or liquid sample. The wavelength of light absorbed is characteristic of the chemical bond. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FT-IR was used to examine possible interactions between the switchgrass based Epon 828 and liquefied bio-oil.

Figure 4.16 shows that hydroxyl groups in the bio-oil had been consumed. And also an Epoxide ring in the Epon 828 disappeared when the new switchgrass based epoxy resin formed which means that the crosslink was built in the new epoxy resins. The characteristic stretching vibration of the peroxide moieties at 914 cm^{-1} (C-O-C) completely disappeared after curing (Abdul Khalil, Marliana et al. 2011). The peak at 1116 cm^{-1} for the bio-oil was further removed when blended and cured with epon and can be attributed to bands observed with variation in lignin (Zhang et al. 2012). A small peak near 1722 cm^{-1} was also observed within the bio-oil which was consumed after blending and cure. Zhang et al. (2012) attribute this to the carbonyl groups that must have participated in the cross-linking reaction. A broad absorption band at 3336cm^{-1} was assigned to aromatic and aliphatic OH groups (Abdul Khalil, Marliana et al. 2011) which disappeared in the FT-IR curve of switchgrass based epoxy resin.

This means that we produced Hydroxyl group successfully and the OH group reacted with Epon 828 to generate the new type of switchgrass based epoxy resin.

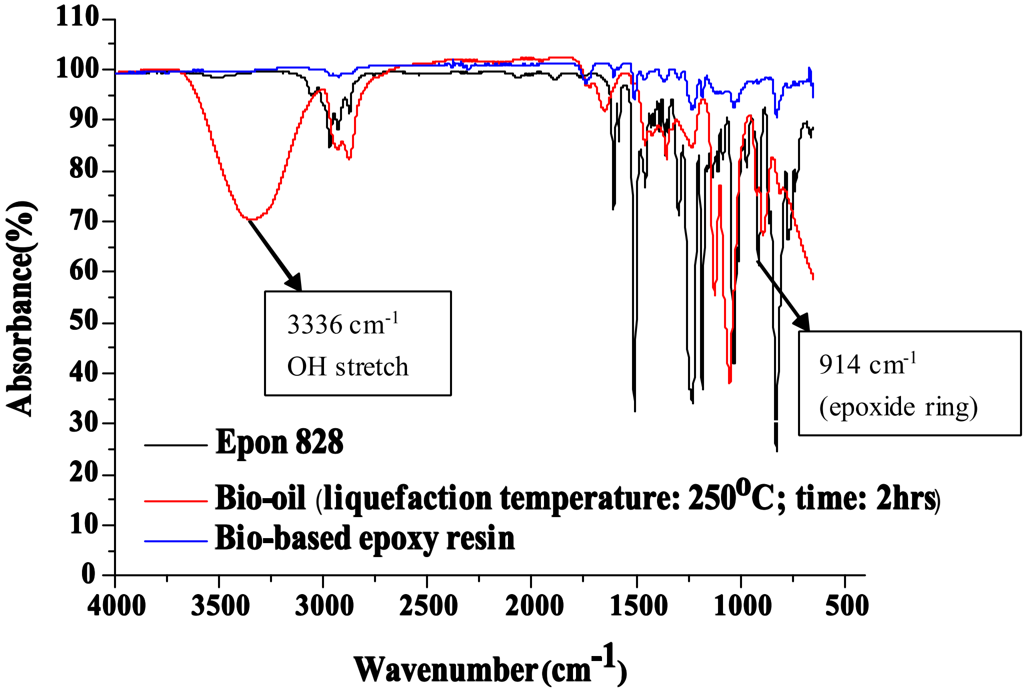


Fig. 4.16 FT-IR graph of Absorbance versus Wavenumber for Epon 828, Bio-oil and bio-oil based epoxy resin.

Figure 4.17 shows that when liquefaction temperature was 250°C and liquefaction time was 2h, the mass ratio of Epon 828 to switchgrass based epoxy resin 1:1 had the lowest OH group which indicates that it has the highest cross linking structure.

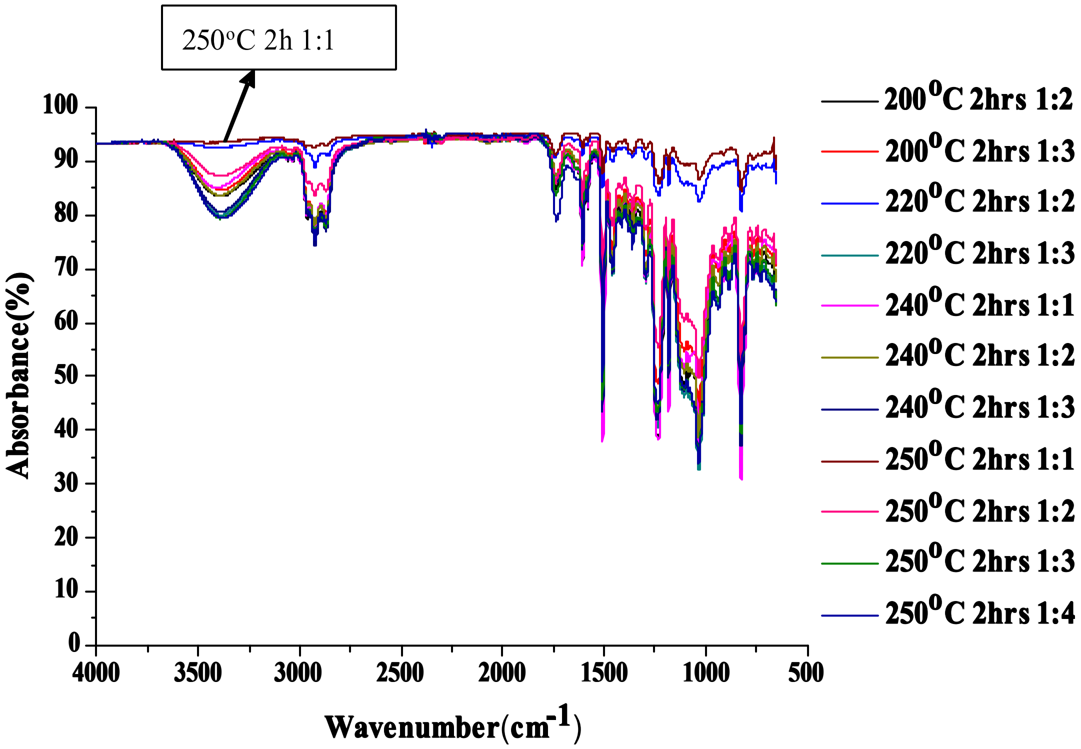


Fig. 4.17 FT-IR graph of Absorbance versus Wavenumbe for switchgrass based epoxy resins when liquefaction time was fixed at 2 h and liquefaction temperature was changed from 200°C to 260°C.

Figure 4.19 shows that when the liquefaction temperature was 250°C and liquefaction time was 2h, the mass ratio of Epon 828 to switchgrass based epoxy resin 1:1 had the lowest OH group which indicates that it has the highest cross linking structure.

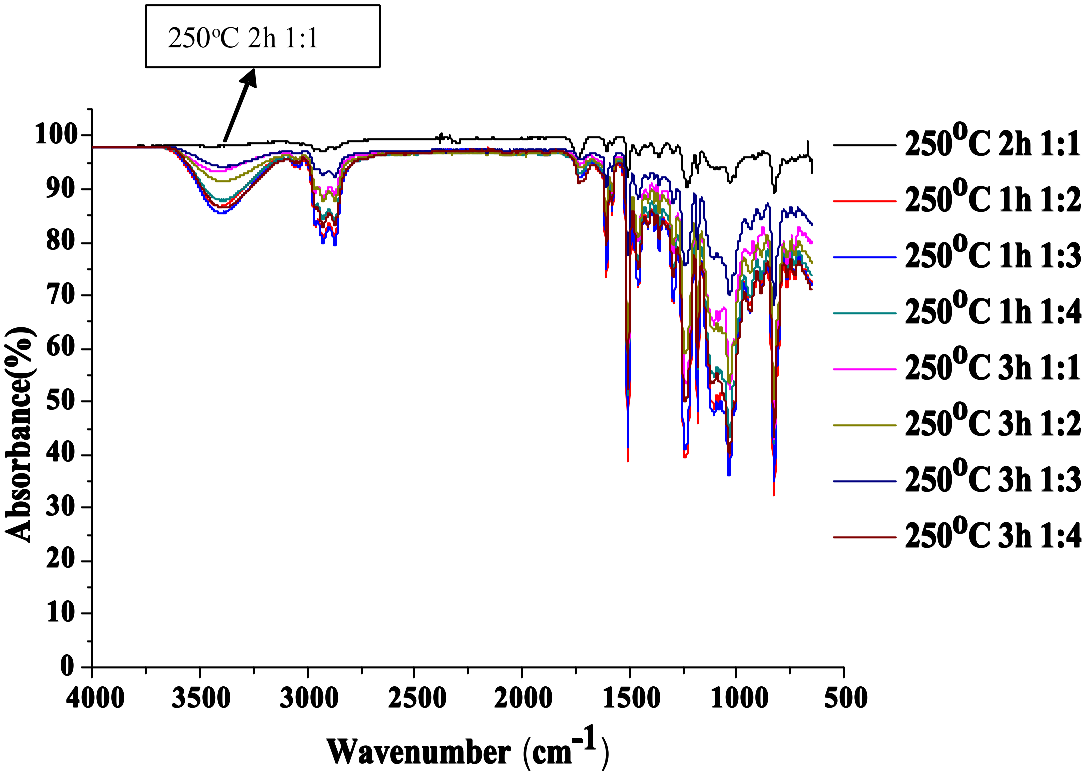


Fig. 4.18 FT-IR graph of Absorbance versus Wavenumber for switchgrass based epoxy resins when liquefaction temperature was fixed at 250°C and liquefaction time was changed from 1 hour to 3 hours.

4.4 Conclusions

The following are experimental results (Table 4.6 and Table 4.7) for the whole experiment.

Table 4.6 Experimental Result I

Ratio(Epon:bio-oil)\Temp		200℃	220℃	240℃	250℃	260℃
Residue Percentage (%)		85.48	68.87	57.3	54.2	50.14
Hydroxyl number (KOH/g)		951.75±6.423.94	941.29±5.41	898.11±3.02	875.32±6.42	947.82±8.77
pH value		3.51	3.81	4.50	5.18	4.83
1:1	Tg (℃)	-	38.44	42.93	62.84	-
	Weight loss (%)	-	-	79.59±0.63	41.89±0.78	-
	Decomposition temp (℃)	-	-	447.08	439.91	-
1:2	Tg (℃)	40.47	48.76	42.68	48.69	-
	Weight loss (%)	61.96 ±0.43	46.48 ±0.34	65.18±0.58	50.63±0.53	-
	Decomposition temp (℃)	442.60	452.46	446.19	444.56	-
1:3	Tg (℃)	37.15	42.41	35.65	35.86	-
	Weight loss (%)	60.94 ±0.86	57.30 ±0.67	71.46±0.81	67.60±0.40	-
	Decomposition temp (℃)	416.59	447.98	450.67	428.25	-
1:4	Tg (℃)	-	-	-	28.25	-
	Weight loss (%)	-	62.00 ±0.41	67.70±0.67	61.40±0.42	-
	Decomposition temp (℃)	-	-	-	409.42	-

The conditions above are based on the reaction time which is 2 h.

Table 4.7 Experimental Result II

Ratio(Epon:bio-oil)		1h	2h	3h
Residue Percentage (%)		82	54.2	72.4
Hydroxyl number (KOH/g)		956.48±11.70	875.32±6.42	953.10±10.58
pH value		5.47	5.19	5.64
1:1	Tg (℃)	-	62.84	62.23
	Weight loss (%)	-	41.89±0.78	54.97±0.61
	Decomposition temp (℃)	-	-	450.67
1:2	Tg (℃)	40.16	48.69	45.64
	Weight loss (%)	59.19 ±0.69	50.63±0.53	50.97±0.72
	Decomposition temp (℃)	447.08	-	439.91
1:3	Tg (℃)	26.81	35.86	40.44
	Weight loss (%)	53.30 ±0.16	67.60±0.40	54.46±0.90
	Decomposition temp (℃)	-	-	441.70
1:4	Tg (℃)	31.02	28.25	35.61
	Weight loss (%)	63.47 ±0.30	61.40±0.42	54.64±0.36
	Decomposition temp (℃)	-	-	-

The conditions above are based on the reaction temperature which is 220°C.

"-" means the status of the test samples were too rubbery to be tested.

The switchgrass based bio-oil contains a number of hydroxyl groups which could be used in the reaction to manufacture a new type of epoxy resin. The switchgrass based bio-oil was successfully reacted with the Epon 828 using the TPP as catalyst.

The optimal liquefaction temperature was 250°C and the optimal liquefaction time was 2 h. The optimal mass ratio of Epon to switchgrass based bio-oil was 1:1 because it had high performance in all kinds of tests including DSC, TGA, Soxhlet extraction and FT-IR.

4.5 Reference

Abdul Khalil, H. P. S., M. M. Marliana, et al. (2011). "Exploring isolated lignin material from oil palm biomass waste in green composites." Materials & Design **32**(5): 2604-2610.

Auad, M. L., Nutt, S. R., Stefani, P. M., & Aranguren, M. I. (2006). "Rheological study of the curing kinetics of epoxy–phenol novolac resin". Journal of applied polymer science, 102(5), 4430-4439.

Auad, M. L., L. Zhao, et al. (2007). "Flammability properties and mechanical performance of epoxy modified phenolic foams." Journal of Applied Polymer Science 104(3): 1399-1407.

Ben, H., & Ragauskas, A. J. (2011). "NMR characterization of pyrolysis oils from Kraft lignin". Energy & Fuels, 25(5), 2322-2332.

Berndes, G., M. Hoogwijk, et al. (2003). "The contribution of biomass in the future global energy supply: a review of 17 studies." Biomass and Bioenergy **25**(1): 1-28.

Delmas, G.-H., B. Benjelloun-Mlayah, et al. (2013). "Biolignin™ based epoxy resins." Journal of Applied Polymer Science 127(3): 1863-1872.

Jasiukaitytė, E., M. Kunaver, et al. (2010). "Lignin behaviour during wood liquefaction—Characterization by quantitative 31P, 13C NMR and size-exclusion chromatography." Catalysis Today 156(1–2): 23-30.

Jasiukaitytė, E., M. Kunaver, et al. (2009). "Cellulose liquefaction in acidified ethylene glycol." Cellulose 16(3): 393-405.

Kimura, H., A. Matsumoto, et al. (1998). "Epoxy resin cured by bisphenol A based benzoxazine." Journal of Applied Polymer Science **68**(12): 1903-1910.

Kishi, H., A. Fujita, et al. (2006). "Synthesis of wood-based epoxy resins and their mechanical and adhesive properties." Journal of Applied Polymer Science **102**(3): 2285-2292.

Kobayashi, M., T. Asano, et al. (2004). "Analysis on residue formation during wood liquefaction with polyhydric alcohol." Journal of Wood Science 50(5): 407-414.

Kumar, S. and R. B. Gupta (2009). "Biocrude Production from Switchgrass Using Subcritical Water." Energy & Fuels **23**(10): 5151-5159.

Kunaver, M., S. Medved, et al. (2010). "Application of liquefied wood as a new particle board adhesive system." Bioresource Technology **101**(4): 1361-1368.

Kurimoto, Y., S. Doi, et al. (1999). Species Effects on Wood-Liquefaction in Polyhydric Alcohols. Holzforschung. **53:** 617.

Littell, J. D., C. R. Ruggeri, et al. (2008). "Measurement of epoxy resin tension, compression, and shear stress-strain curves over a wide range of strain rates using small test specimens." Journal of Aerospace Engineering **21**(3): 162-173.

Liu, Y.-L., G.-H. Hsiue, et al. (1997). "Synthesis, characterization, thermal, and flame retardant properties of phosphate-based epoxy resins." Journal of Polymer Science Part A: Polymer Chemistry **35**(3): 565-574.

Lourdin, D., Coignard, L., Bizot, H., & Colonna, P. (1997). “Influence of equilibrium relative humidity and plasticizer concentration on the water content and glass transition of starch materials”. Polymer, 38(21), 5401-5406.

Ma, X. J. and G. J. Zhao (2008). "Structure and performance of fibers prepared from liquefied wood in phenol." Fibers and Polymers **9**(4): 405-409.

Mansouri, N. E., Yuan, Q., & Huang, F. (2011). “Characterization of alkaline lignins for use in phenol-formaldehyde and epoxy resins”. BioResources, 6(3), 2647-2662.

Mei Zhen, G., G. Da Chun, et al. (2010). “Study on the effect of fractionation pretreatment process on the enzymatic hydrolysis of switch grass for bioenergy and biorefinery”. Advances in Energy Engineering (ICAEE), 2010 International Conference on.

Nonaka, Y., Tomita, B., & Hatano, Y. (1997). “Synthesis of lignin/epoxy resins in aqueous systems and their properties”. Holzforschung, 51(2), 183-187.

Pan, H., Zheng, Z., & Hse, C. Y. (2012). “Microwave-assisted liquefaction of wood with polyhydric alcohols and its application in preparation of polyurethane (PU) foams”. European Journal of Wood and Wood Products, 70(4), 461-470.

Pan, H., T. F. Shupe, et al. (2007). "Characterization of liquefied wood residues from different liquefaction conditions." Journal of Applied Polymer Science **105**(6): 3740-3746.

Pan, H., T. F. Shupe, et al. (2008). "Synthesis and cure kinetics of liquefied wood/phenol/formaldehyde resins." Journal of Applied Polymer Science **108**(3): 1837-1844.

Prassianakis, I. N., V. Kytopoulos, et al. (2006). "Investigation of mechanical properties of epoxy resins and random fibre epoxy systems by means of destructive and non-destructive tests." International Journal of Materials & Product Technology 26(1-2): 105-121.

Rezzoug, S.-A. and R. Capart (2002). "Liquefaction of wood in two successive steps: solvolysis in ethylene-glycol and catalytic hydrotreatment." Applied Energy 72(3–4): 631-644.

Sun, P., Heng, M., Sun, S. H., & Chen, J. (2011). “Analysis of liquid and solid products from liquefaction of paulownia in hot-compressed water”. Energy Conversion and Management, 52(2), 924-933.

Thangalazhy-Gopakumar, S., Adhikari, S., Ravindran, H., Gupta, R. B., Fasina, O., Tu, M., & Fernando, S. D. (2010). “Physiochemical properties of bio-oil produced at various temperatures from pine wood using an auger reactor”. Bioresource technology, 101(21), 8389-8395.

Vanin, F. M., Sobral, P. J. A., Menegalli, F. C., Carvalho, R. A., & Habitante, A. M. Q. B. (2005). “Effects of plasticizers and their concentrations on thermal and functional properties of gelatin-based films”. Food Hydrocolloids, 19(5), 899-907.

Wang, H., & Chen, H. Z. (2007). “A novel method of utilizing the biomass resource: Rapid liquefaction of wheat straw and preparation of biodegradable polyurethane foam (PUF)”. Journal of the Chinese Institute of Chemical Engineers, 38(2), 95-102.

Wu, C.-C. and W.-J. Lee (2010). "Synthesis and properties of copolymer epoxy resins prepared from copolymerization of bisphenol A, epichlorohydrin, and liquefied Dendrocalamus latiflorus." Journal of Applied Polymer Science 116(4): 2065-2073.

Yamada, T. and H. Ono (2001). "Characterization of the products resulting from ethylene glycol liquefaction of cellulose." Journal of Wood Science 47(6): 458-464.

Yao, Y., M. Yoshioka, et al. (1996). "Water-absorbing polyurethane foams from liquefied starch." Journal of Applied Polymer Science 60(11): 1939-1949.

Xie, T. and F. G. Chen (2005). "Fast liquefaction of bagasse in ethylene carbonate and preparation of epoxy resin from the liquefied product." Journal of Applied Polymer Science 98(5): 1961-1968.

Zheng, Z., Pan, H., Huang, Y., Chung, Y., Zhang, X., & Feng, H. (2011). “Rapid Liquefaction of Wood in Polyhydric Alcohols Under Microwave Heating and its Liquefied Products for Preparation of Rigid Polyurethane Foam”. Open Materials Science Journal, 5, 1-8.

Zhang, H., Ding, F., Luo, C., Xiong, L., & Chen, X. (2012). “Liquefaction and characterization of acid hydrolysis residue of corncob in polyhydric alcohols”. Industrial Crops and Products, 39, 47-51.