May 2015

Synthesis, Characterization and Applications of Lignin-Based Epoxy Resins

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Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF LIGNIN-BASED EPOXY RESINS

(Thesis format: Integrated Article)

by

Fatemeh Ferdosian

Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

The School of Graduate and Postdoctoral Studies

The University of Western Ontario

London, Ontario, Canada

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Abstract
Epoxy resin is one of the most versatile thermosetting polymers with diverse applications. Epoxy resins are mainly produced from the reaction of bisphenol-A (BPA) and epichlorohydrin. The consumption of bisphenol-A is facing growing concerns over its carcinogenic effects and its sustainability. Lignin can be a promising renewable substitute of bisphenol-A in the synthesis of epoxy resins.

In this thesis work, a novel method has been developed for the synthesis of bio-based epoxy resins with reduced side reactions, employing de-polymerized lignin from organosolv lignin (DOL), kraft lignin (DKL) and hydrolysis lignin (DHL) under alkaline condition in the presence of a phase transfer catalyst, tetrabutylammonium bromide (TBAB). The preliminary results showed that the reaction temperature, reaction time, NaOH/lignin molar ratio and epichlorohydrin/lignin molar ratio influenced the reaction yield and the molecular weights of the final products. The synthesis process has been optimized by using response surface methodology to produce bio-based epoxy resins with a higher epoxy content and greater yield. Under the optimum conditions using DOL, DOL-based epoxy resins with an epoxy content as high as ~8 was produced at 99% yield. The synthesis using DKL at the optimum conditions led to a DKL-based epoxy resin with an epoxy content of 5.6 at 97% yield. In addition, bio-based epoxy resins derived from hydrolysis lignin (HL) have also been synthesized with lower amount of catalyst using DHL. The DHL-epoxy resin obtained at the optimum conditions has an epoxy content of ~5 and 95% yield.

The curing kinetics of admixtures of the synthesized lignin-based epoxy resins and a conventional BPA-based epoxy resin at various blending ratios were investigated using differential scanning calorimetry (DSC) with two kinds of curing agents, i.e. diaminodiphenyl methane (DDM), diethylenetriamine (DETA). The kinetic parameters were evaluated by the model-free kinetics and the activation energy for the curing reaction was calculated as a function of conversion. The activation energy changed with the progress of curing process and it revealed that the curing of a lignin-based epoxy resin is a complex process with several reactions occurring at the same time. The fluctuation of activation energy depended on the content of the lignin-based epoxy resin in the blended mixture, type of lignin-based epoxy resin and the type of curing agent used.

The synthesized lignin-based epoxy resins were blended with a conventional BPA-based epoxy resin at a blending ratio of 0-100wt.% and used as polymer matrixes for manufacturing fiber
reinforced plastics (FRPs). The thermal stability of the obtained lignin-based epoxy resins was also characterized using TGA-FTIR analysis. The mechanical/thermal characterization results indicated that the lignin-based epoxy resins have excellent mechanical/thermal properties and can be used as a substitute for conventional BPA-based epoxy resins at a ratio up to 75 wt% in FRPs without compromising their properties.

**Keywords**

Epoxy resin, de-polymerized organosolv lignin (DOL), de-polymerized kraft lignin (DKL), de-polymerized hydrolysis lignin (DHL), lignin-based epoxy resin, synthesis, optimization, diaminodiphenyl methane (DDM), diethylenetriamine (DETA), curing kinetics, model-free kinetics, activation energy, fiber reinforced plastic (FRP), mechanical properties, thermal stability, thermal decomposition.
Co-authorship Statement

Chapter 3: Chemically Modified Lignin through Epoxidation and its Thermal Properties.

This chapter is a combination of the following two publications:


The experiment work was conducted by Fatemeh Ferdosian under the supervision of Prof. Charles (Chuanbao) Xu and Dr. Mark Anderson and the guidance of Dr. Zhongshun Yuan. Writing and data analysis of these publications were conducted by Fatemeh Ferdosian. It was reviewed and revised by Prof. Charles Xu, Dr. Mark Anderson and Dr. Zhongshun Yuan.


This chapter is a combination of the following two publications:


The experiment work was conducted by Fatemeh Ferdosian under the supervision of Prof. Charles (Chuanbao) Xu and Dr. Mark Anderson and the guidance of Dr. Zhongshun Yuan. Writing and data analysis of these publications were conducted by Fatemeh Ferdosian. It was reviewed and revised by Prof. Charles Xu, Dr. Mark Anderson and Dr. Zhongshun Yuan.
Chapter 5: Sustainable Lignin-based Epoxy Resins Cured with Aromatic and Aliphatic Amine Curing Agents: Curing Kinetics and Thermal Properties.

Authors: Ferdosian, F., Yuan, Z., Anderson, M. and Xu, C.

The experiment work was conducted by Fatemeh Ferdosian under the supervision of Prof. Charles (Chuanbao) Xu and Dr. Mark Anderson, and the guidance of Dr. Zhongshun Yuan. Writing and data analysis of these publications were conducted by Fatemeh Ferdosian. It was reviewed and revised by Prof. Charles Xu, Dr. Mark Anderson and Dr. Zhongshun Yuan. The manuscript is ready for submission to “Green Chemistry”.

Chapter 6: Curing Kinetics and Mechanical Properties of Fiber Reinforced Composites Comprising Glass Fibers and Lignin-Based Epoxy.

Authors: Ferdosian, F., Zhang, Y., Yuan, Z., Anderson, M. and Xu, C.

The experiment work was conducted by Fatemeh Ferdosian under the supervision of Prof. Charles (Chuanbao) Xu and Dr. Mark Anderson, and the guidance of Dr. Zhongshun Yuan. Writing and data analysis of these publications were conducted by Fatemeh Ferdosian with assisted from Dr. Yongsheng Zhang. It was reviewed and revised by Prof. Charles Xu, Dr. Mark Anderson and Dr. Zhongshun Yuan. The manuscript is ready for submission to “Polymer”.

Chapter 7: Thermal Performance and Thermal Decomposition Kinetics of Lignin-Based Epoxy Resins

Authors: Ferdosian, F., Yuan, Z., Anderson, M. and Xu, C.

The experiment work was conducted by Fatemeh Ferdosian under the supervision of Prof. Charles (Chuanbao) Xu and Dr. Mark Anderson, and the guidance of Dr. Zhongshun Yuan. Writing and data analysis of these publications were conducted by Fatemeh Ferdosian. It was reviewed and revised by Prof. Charles Xu, Dr. Mark Anderson and Dr. Zhongshun Yuan. The manuscript is ready for submission to “Polymer Degradation and Stability”.

Chapter 8: Synthesis and Characterization of Hydrolysis Lignin-based Epoxy Resins

Authors: Ferdosian, F., Yuan, Z., Anderson, M. and Xu, C.
The experiment work was conducted by Fatemeh Ferdosian under the supervision of Prof. Charles (Chuanbao) Xu and Dr. Mark Anderson, and the guidance of Dr. Zhongshun Yuan. Writing and data analysis of these publications were conducted by Fatemeh Ferdosian. It was reviewed and revised by Prof. Charles Xu, Dr. Mark Anderson and Dr. Zhongshun Yuan. The manuscript is ready for submission to “Green Chemistry”.
Dedication

To

My beloved husband, Ehsan,

&

My wonderful parents, Mohammadsadegh & Dina,

For their endless love, encouragement, and support.
Acknowledgements

Many people have supported me during the completion of this thesis with insightful criticism, assistance, and expertise. This thesis would have never been possible without them.

I would like to express my sincere gratitude to my supervisors Professor Charles (Chuanbao) Xu at Western University and Dr. Mark Anderson at Arclin Company for their valuable guidance, continuous support, encouragement, advice and help throughout my PhD study.

My sincere appreciation is extended to Dr. Zhongshun (Sean) Yuan for his priceless feedback, advice and guidance in the transition and completion of this research project. In addition, I would like to thank my PhD supervision committee members, Dr. Cedric Briens and Dr. Franco Berruti, from the Institute for Chemicals and Fuels from Alternative Resources (ICFAR), for their comments and suggestions.

I also gratefully acknowledge the financial support provided by the University of Western Ontario Graduate Studies, the Department of chemical and Biochemical Engineering at the University of Western Ontario (Teaching Assistantship, Graduate Research Scholarship), NSERC/FPIInnovations Industrial Research Chair Program in Forest Biorefinery and the Ontario Research Fund-Research Excellence (ORF-RE) from Ministry of Economic Development and Innovation as well as the MITACS Accelerate Program. Support from the industrial partners including FPIInnovations and Arclin Canada is also acknowledged.

I would also like to thank Caitlin Marshall, Fang (Flora) Cao, Thomas Johnston, Dr. Wei Wu, Dr. Ying Fan and Lem Gabrehiwet for their contributions and assistance in analyzing and characterization of my samples.

I thank my fellow colleagues at ICFAR for their assistance and friendship: Malaya Nanda, Yongsheng (Ryan) Zhang, Shanghuan (Shawn) Feng, and Bing Li.

My deepest appreciation and sincere gratitude goes to my family, without whom I would have never been able to reach this point. Words cannot express how grateful I am to my parents for their
love and support. At last, I would like to gratefully thank my beloved husband, Ehsan Ghiasi, for his patience, care, unconditional love, encouragement and support during all these years.

Fatemeh Ferdosian
Western University
April 2015
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<tbody>
<tr>
<td>CCD</td>
<td>Central Composite Design</td>
</tr>
<tr>
<td>DDM</td>
<td>Diaminidiphenyl Methane</td>
</tr>
<tr>
<td>DETA</td>
<td>Diethylenetriamine</td>
</tr>
<tr>
<td>DHL</td>
<td>De-polymerized Hydrolysis Lignin</td>
</tr>
<tr>
<td>DGEBA</td>
<td>Diglycidyl Ether of Bisphenol A</td>
</tr>
<tr>
<td>DKL</td>
<td>De-polymerized Kraft Lignin</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analysis</td>
</tr>
<tr>
<td>DOL</td>
<td>De-polymerized Organosolv Lignin</td>
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<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EC</td>
<td>Epoxy Content (weight percent epoxide)</td>
</tr>
<tr>
<td>ECH</td>
<td>Epichlorohydrin</td>
</tr>
<tr>
<td>EEW</td>
<td>Epoxied Equivalent Weight (g/eq)</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>FWO</td>
<td>Flynn-Wall-Ozawa Model</td>
</tr>
<tr>
<td>GC-TCD</td>
<td>Gas Chromatography- Thermal Conductivity Detector</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
</tr>
<tr>
<td>HL</td>
<td>Hydrolysis Lignin</td>
</tr>
<tr>
<td>HNMR</td>
<td>Proton Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>KL</td>
<td>Kraft Lignin</td>
</tr>
<tr>
<td>OL</td>
<td>Organosolv Lignin</td>
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<tr>
<td>PDI</td>
<td>Polydispersity Index</td>
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<tr>
<td>RSM</td>
<td>Response Surface Method</td>
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<td>$T_g$</td>
<td>Glass transition temperature (°C)</td>
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<td>$M_c$</td>
<td>Average molar mass between crosslinks (g/mol)</td>
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<td>$G_e$</td>
<td>Equilibrium modulus in the rubbery region (MPa)</td>
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Chapter 1

General Introduction
1.1 Introduction

The main aim of this PhD project was to develop a novel method for the synthesis of bio-based epoxy resins using lignin as a substitute for bisphenol-A (BPA). The mechanical and thermal properties of synthesized lignin-based epoxy resins were examined to demonstrate its potential in manufacturing of fiber reinforced plastics (FRPs).

1.2 Background

Polymers are playing an important role in our daily lives in many ways, and its consumption has consistently grown in the past decade and was approximately 268 million tons in 2007 [1]. One key issue towards polymer applications is that currently the depleted fossil fuel resources are the predominant sources for raw materials in the production of polymers. The huge consumption of fossil resources leads to sustainability and environmental issues. The main concern is associated with global warming and climate change [2,3]. Another concern of synthetic polymers is the natural degradation rate of the polymeric materials, highly resistant to bio-degradation, which has resulted in the increase of the polymeric wastes in the environment [1]. The ultimate concern about the increasing production of petroleum-based polymers is the depletion of fossil resources and the limited access to these resources in the future, which would undoubtedly increase the prices of the polymers. The increasing concerns over the environmental issues and the sustainability of the petroleum-based chemical and material products have intensified the interest in the design and development of new bio-based chemicals and materials using renewable resources [4]. The immense availability and unique functionality of renewable resources can potentially make it possible to reduce the cost and improve the properties of the existing chemical/material products [5].

Epoxy resins were first discovered in 1938 by a Swiss chemist [6] and commercialized in 1946 [7]. Epoxy resins are one of the most versatile materials due to their unique properties such as good chemical resistance, high moisture and solvent resistances, good thermal and dimensional stabilities, high adhesion strength and superior electrical properties. These properties provide diverse applications for epoxy resins, in such fields as high performance composites, industrial coatings, adhesives, electrical-electronic laminates, flooring and paving applications, etc. [8–10].
Based on the Global Industry Analysts (GIA) announcement, the global market of epoxy resins will reach over 3 million tons by 2017 [11].

Biomass is an immense renewable resource that has the potential to substitute petroleum for sustainable production of bio-energy and bio-based chemicals/materials [1]. Lignin is the second most abundant natural renewable polymer after cellulose [12,13] and accounts for 15-30 wt.% of lignocellulosic biomass (such as woody biomass, crop residues, etc.). Lignin represents 30 wt.% of all non-fossil organic carbon on the earth. The availability of lignin is around 300 billion tons which increases annually by 20 billion tons [14]. Lignin (mainly kraft lignin, KL) has been considered as a waste by-product in paper pulping processes. Annual generation of lignin in the paper pulping industry is estimated to be over 70 million tons worldwide [5]. Lignin is mainly consumed in the mills for heat and power generation. The annual sales of lignin as special chemicals (mainly lignosulfonates) amount to a mere 1% of total lignin produced from various sources [13]. To use lignin as a substitute for petroleum-based chemicals in the manufacture of synthetic polymers will yield both economical and environmental dividends. However, there are two main obstacles that limit the applications of crude lignin in materials: (1) industrial lignin from the pulping process has a molecular weight too high to be useful as raw materials for polymer synthesis, and (2) lignin has low compatibility with other polymers. Chemical modification of lignin can overcome the above obstacles, producing materials with appropriate molecular weight and improved compatibility.

1.3 Research Objectives

As discussed above, it is essential to find alternative and renewable resources to replace petroleum for the production of chemicals and materials. Lignin is one of the most abundant natural polymeric materials on earth after cellulose. The availability and functionality of lignin provide the possibility to use it as phenolic or polyol feedstock for the synthesis of various polymers and composites. However, only a small portion of lignin has found industrial applications in chemical/material production. The main obstacles that limits the applications of crude lignin in chemicals and polymer synthesis are its large molecular weight and low compatibility with other polymers. Thus, chemical modifications of crude lignin are required.
Among the many options for adding lignin to epoxy resins, the glycidylation pre-treatment provides the best assurance for covalent incorporation of lignin into the network structure upon curing of the resin. The functionalization of lignin with glycidyl ether groups by reaction with epichlorohydrin (in alkali condition) is the basis for the synthesis of crosslinkable epoxy functional lignin derivatives.

When epoxidizing lignin, one has to overcome some challenges intrinsic to lignin, e.g., many types of technical lignin are insoluble in organic solvents and lignin bears a range of hydroxyl groups with non-uniform reactivity. Chemical modification can be a promising solution to these problems. The main objective of this research is to cost-effectively produce bio-based epoxy resin from lignin, by first epoxidizing de-polymerized lignins (with lower molecular weights), as illustrated in Figure 1-1.

![Monomers of Lignin](image.png)

**Figure 1-1** Production of lignin-based epoxy resins.

1.4 Approaches and Methodology

Technical lignin has a high average molecular weight and some types of lignin such as kraft lignin and hydrolysis lignin are not soluble in common organic solvents, which makes it difficult to be used as a substitute for petroleum-based chemicals for the synthesis of bio-based polymer materials, e.g., epoxy resins, at a high substitution ratio. Therefore, the original lignins including organosolv lignin, kraft lignin and hydrolysis lignin were firstly de-polymerized into the low molecular weight
feedstock. The de-polymerization reaction was conducted in a 500ml Parr stirred autoclave reactor. Figure 1.2 displays the reactor used in this research.

![500ml autoclave reactor system used for de-polymerization of lignin.](image)

**Figure 1-2:** 500ml autoclave reactor system used for de-polymerization of lignin.

The de-polymerized lignins were used as a feedstock for synthesis of lignin-based epoxy resins by reacting the de-polymerized lignin with epichlorohydrin in a three-neck glassware reactor under a variety of reaction conditions. Based on the literature [15–17], there are many parameters that affect the lignin epoxidation reaction, as illustrated in Figure 1-3.
Figure 1-3 Process parameters affecting the epoxidation reaction.

The structure of the obtained lignin-based epoxy resins were characterized with different analytical methods including Fourier Transform Infrared Spectroscopy (FTIR) and Proton Nuclear Magnetic Resonance (H-NMR) spectroscopy to confirm the grafting of epoxy groups onto the lignin structure, and the titration method to measure the epoxy content (EC, weight percent epoxide) and epoxide equivalent weight (EEW, g/eq) in accordance to the standard test method ASTM D1652-16. In titration method, the resins dissolved in 30 mL of methylene chloride (MECL) and 15 mL of tetraethylammonium bromide (TEAB) solution in acetic acid, then the resulting solution is titrated with perchloric acid solution. As the reaction progresses, the potential of the solution gradually increases until the reaction approaches to completion at which point the potential increases very quickly. This equivalence point of titration was used to calculate the epoxy content (EC) and epoxide equivalent weight (EEW) of resin as follows:

\[
EC = \frac{4.3 \times V \times N}{W}
\]  

(1-1)

\[
EEW = \frac{43 \times 100}{EC}
\]  

(1-2)
Where $V$ is the actual mL perchloric acid used to reach equivalence point, $N$ is normality of perchloric acid reagent, $W$ is the weight of the sample used and 4.3 is the theoretical molecular weight of the epoxide ring, 43, and it is adjusted to 4.3 for the calculation to percent epoxide.

For the production of bio-based epoxy composites or coating materials, the epoxy content of the synthesized epoxy resins needs to be determined to decide the stoichiometric ratio of the lignin-epoxy/hardener in the curing process which is believed to strongly impact on the properties of the final materials[18]. For instance, adding a hardener in an amount greater than the stoichiometric ratio would lead to excess hardener materials remaining as low molecular components in the cured product, lowering the glass transition temperature of the cured materials. On the other hand, adding insufficient hardener for fully cure would decrease the materials strength. Hence, the epoxy content of the synthesized lignin-epoxy was accurately quantified in this work.

Amines, polyamides, phenolic resins, anhydrides, isocyanates and polymercaptans are common curing agents (or hardeners) for epoxy resins [6,19]. The choice of hardeners depends on the application, the process selected, and the desired properties. Both aromatic and aliphatic amines can be chosen as superb curing agents for epoxy resins. Aromatic amines are usually used to cure epoxy resins for the applications in composites, molding compounds, and castings but the aliphatic amines are more suitable for adhesive and coating applications [20]. In this work, the kinetics and mechanism of curing reaction of the lignin-epoxy resins and the curing agent were also studied by Differential Scanning Calorimetry (DSC). Moreover, the thermal and mechanical properties of the cured bio-composites were characterized by Thermo-gravimetric Analysis (TGA), Universal Testing Machine (UMT) and Dynamic Mechanical Analysis (DMA).

1.5 Thesis Overview

The thesis consists of eight chapters organized in the following sequence:

Chapter 1 provides a general introduction to the importance of synthesis of lignin-based epoxy resin as a bio-based polymer with a great industrial and environmental potential. The research objectives, approach and methodology, and thesis structure are outlined.

Chapter 2 presents a detailed overview of the available literature on synthesis of bio-based epoxy resin and its characteristics with the main focus on lignin-based epoxy resins. The commercial
method of synthesis of petroleum based epoxy resins and application of epoxy resins are also described in this chapter.

**Chapter 3** provides an investigation of the feasibility of synthesis of bio-based epoxy resins from organosolv lignin. The effect of the process parameters on the average molecular weight and the yield of epoxy grafting reaction were studied. The thermal properties of the synthesized samples were also compared.

**Chapter 4** investigates the effect of synthesis variables including reaction time, reaction temperature and concentration of catalyst on the product yield and epoxy content of lignin-based epoxy resin. These parameters were evaluated by central composite design (CCD) to optimize the effects of these parameters. Mathematical correlations were derived from the CCD to show the effects and interaction of these factors on the responses, and the mathematical correlations were used to predict the optimum condition of lignin epoxidation.

**Chapter 5** presents results of a kinetics study on curing of lignin-based epoxy resin with two different curing agents (i.e., aliphatic and aromatic amine). The bio-based epoxy resins were synthesized from de-polymerized organosolv lignin and de-polymerized kraft lignin in optimum conditions obtained from previous study presented in Chapter 4. The lignin-based epoxy resins curing kinetics were studied using differential scanning calorimetry (DSC), and the DSC results were evaluated by Kissinger model to calculate the apparent activation energy and two isoconversional models, i.e. Friedman and another advanced method proposed by Vyazovkin to determine the trend of activation energy during the curing process. In addition, thermogravimetric analysis (TGA) was employed to investigate the thermal stabilities of the cured lignin-based epoxy resins.

**Chapter 6** focuses on the curing kinetics and mechanical properties of glass fiber reinforced plastics (FRPs) comprising blends of a lignin-based epoxy resin and a convention BPA-based epoxy resin at a blending ratio of 0-100 wt%. Stoichiometric amount of diaminodiphenylmethane (DDM) was used as the curing agent. The curing kinetics were evaluated by the model free kinetics and the dominant reactions were proposed in each specific stage of reaction. The tensile and flexural properties of the FRPs were studied using a universal testing machine (UTM) to determine the optimum blending ratio for the lignin-based epoxy resin in the bio-composite formulation.
Chapter 7 describes the thermal stability of the DDM-cured resin blends of a DKL or DOL-based epoxy resin and a convention BPA-based epoxy resin at different blending ratios (0-100 wt%). A TGA-FTIR coupled system was employed to determine the thermal decomposition temperature (by TGA) and qualitative composition of the gas evolved (by FTIR) from heating the resin blends. A mechanism of thermal decomposition of lignin-based epoxy resins was proposed based on the activation energy during the thermal decomposition process.

Chapter 8 describes the production of a bio-based epoxy resin using de-polymerized hydrolysis lignin (DHL). The curing kinetic of the DHL-based epoxy resins was examined by DSC. Furthermore, the thermomechanical performances of the resins were studied to demonstrate the potential of substituting bisphenol-A with DHL in the synthesis of bio-based epoxy resins.

Chapter 9 presents the main conclusions obtained from the present research and suggests future studies.
1.6 References


Chapter 2

Literature Review
In this chapter, some general information about the chemistry and application of epoxy resin is provided. Following a brief overview of bio-refinery, lignin and its chemical structure are discussed. In addition, the available literature on bio-based epoxy resin is reviewed. Most of the information is related to lignin-based epoxy resins, which is the main focus of this research. The results of synthesis of other bio-based epoxy resins have also been included in the discussion where relevant. Moreover, curing kinetics and the mechanical and thermal properties of lignin-based epoxy resins are discussed.

2.1 Epoxy Resins

Epoxy resin is defined as a component with the average of more than one epoxy group per molecule [1]. The common glycidyl epoxy resin is usually synthesized in a reaction of bisphenol-A with epichlorohydrin [2,3]. Figure 2-1 shows the general structure of epoxy resin. With increasing the number of repeat unit “n” in the epoxy polymer, the physical state of epoxy resin could transform from liquid resins to solid ones. On the other word, the weight-average molecular weight of 380 is liquid at ambient temperature, while an epoxy resin with the weight-average molecular weight of 1000 would be solid at room temperature.

![Chemical structure of epoxy resin.](image)

**Figure 2-1** Chemical structure of epoxy resin.

2.2 The Chemistry of Epoxy Resin Synthesis

At present, 80-90% of commercial epoxy resins are prepared by the reaction of bisphenol-A and epichlorohydrin. The grafting of epoxy groups on phenolic hydroxyl groups (AR-OH) takes place through the reactions as illustrated in Figure 2-2 [4].
NaOH is used as a catalyst for the nucleophilic ring-opening of the epoxide group on the primary carbon atom of epichlorohydrin and as a dehydrochlorinating agent for conversion of the chlorohydrins to epoxide group [5]. Also quaternary ammonium salts (QAS) and phosphonium salts can be used a catalyst to promote the condensation reaction of epichlorohydrin with bisphenol-A [5]. Besides the major reaction of epoxy resins production, some side reactions can take place and may have an effect on the final properties of epoxy resins. The side reactions, as shown as bellow, should be prevented by optimization of reaction conditions [3]:

1. Hydrolysis of epoxy groups

2. Formation of bound chlorine

   a. Reaction of epichlorohydrin with secondary alcohol
b. Abnormal addition of phenolic hydroxyl

\[
\begin{align*}
\text{phenolic hydroxyl} & \quad + \quad \text{epichlorohydrin} \\
\text{produces epoxy resin}
\end{align*}
\]

3. Incomplete dehydrochlorination

The effective factors that influence the properties of low molecular weight epoxy resin were investigated by Krol et al. [6]. These factors are reaction time, reaction temperature, propan-2-ol presence, quantities of water present in the mixture. The optimal conditions for the epoxy resin synthesis were determined to be: 40°C, 90 min reaction time, 5.5 wt. % adding amount of water, 16 wt. % adding amount of 2-propanol additive, with 45% NaOH aqueous solution as a catalyst. Another factor that has marked effect on molecular weight of the obtained epoxy resins is molar ratio of epichlorohydrin/bisphenol-A. An excess of epichlorohydrin is usually used to control the molecular weight of the resin products[4]. The effects of molar ratio of epichlorohydrin on molecular weight and softening point of epoxy resins are presented in Table 2-1.

**Table 2-1** Effects of molar ratio epichlorohydrin/bisphenol A on molecular weight and softening point of epoxy resins [7,8].

<table>
<thead>
<tr>
<th>Molar ratio of epichlorohydrin : bisphenol-A</th>
<th>Molecular weight (M_w) (g/mol)</th>
<th>Epoxide equivalent a</th>
<th>Softening point (°C)</th>
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<td>370</td>
<td>192</td>
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<tr>
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<tr>
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<td>1.2:1</td>
<td>1420</td>
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a pure diglycidyl ether (mol. Wt. 340) with two epoxy groups per molecule, epoxide equivalent=340/2=170
2.3 Curing Agents for Epoxy Resins

A wide range of reagents could react with epoxy resins to form three-dimensional cross-linked thermoset structures [9]. The common curing agents for epoxy resins include amines (aliphatic amine, aromatic amine and modified amines), polyamide resin, imidazoles, polymericcaptan and anhydrides [10,11]. An example amine is 4,4’-Diaminodiphenyl Methane (DDM) whose structure is illustrated in Figure 2-3:

![Chemical structure of 4,4’-Diaminodiphenyl Methane (DDM).](image)

**Figure 2-3** Chemical structure of 4,4’-Diaminodiphenyl Methane (DDM).

Figure 2-4 displays the effects of some amine curing agents on physical properties of epoxy resin systems.

Epoxy resins have tendency to form cured structure by reacting between itself in the presence of an anionic and cationic catalyst. This reaction is known as catalytic homopolymerization. The homopolymerization reaction leads to generation of the polyether systems with great thermal and chemical resistance. The homopolymerization of epoxy occurs at a high temperature and the obtained network is however very brittle, thus with limited applications [3].
| Color     | Viscosity | Pot Life | Low-Temp. Cure | Surface Film | Flexibility | Film Adhesion | Chemical Resistance 
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Figure 2.4 Effects of curing agent (amine curing agents) on some physical properties of epoxy resins. A: Adduct-type curative, MB: Mannich-based-type curative [12].

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Figure 2.4 Effects of curing agent (amine curing agents) on some physical properties of epoxy resins. A: Adduct-type curative, MB: Mannich-based-type curative [12].

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2.4 Application of Epoxy Resins

Epoxy resin is one of the most popular synthetic thermosetting polymers owing to its superior properties such as great chemical resistance, high adhesion strength to various substrates, low curing contraction, high moisture and solvent resistances, good thermal and dimensional stabilities and superior electrical properties [13–15]. These properties provide diverse applications of epoxy resins, which are summarized as follows [3,7,9,16–19]:

1) **Adhesives and bonding:**
The epoxy resins were firstly recognized as adhesive by Preiswerk and Gams in 1944 [3]. The outstanding bonding properties of epoxy resins are associated with the low shrinkage of epoxy resins during the curing process, which causes low internal stress in adhesive joints. Modern adhesive technologies have developed many kinds of epoxy based adhesive systems with variable specification to cover all usages. The epoxy-based adhesives are produced in various forms: room-temperature-curing two-component liquids, heat-curing liquids, powders, hot-melt adhesives, films and tapes [3,7]. Approximately 5% of the total production of epoxy resins is consumed in the adhesive field.

2) **Surface (protective) coatings:**

The large quantities of epoxy resin production are for coating applications. Epoxy resin has great strength bonds to almost all substrates and the formed thin-layer shows good mechanical properties and great chemical and corrosion resistance. Amine curatives have been suggested to be the best hardener for epoxy resins in coating applications [7]. The epoxy-resin coating systems are available in various forms including liquid resins, solid resins (such as fusion bonded epoxy coating (FBE)), high molecular weight thermoplastic resins, radiation curable resins, and special purpose resins [3,7]. More than 60% of the global production of epoxy resin is used in the coatings industry. Approx. 30% of these applications is related to elevated-molecular weight epoxy resins [epoxy value (EV) \( = 0.11-0.02 \text{ mol/100 g, } M_n = 1000-4000 \)], which are mostly used in baking varnishes and powder coatings [20].
3) **Electrical and electronic applications:**

Epoxy resins are commonly used in electrical applications such as castings, pottings, encapsulations, impregnations, coatings, sealants, moldings, etc. The wide application of epoxy resins in electrical industry is attributed to its excellent insulation property, flexibility, fast curing at room temperature, and high chemical and moisture resistance [3].

4) **Composites (reinforced resins):**

Epoxy resins is also used as a polymer matrix in fiber reinforced plastics (FRPs), where the strength and stiffness of epoxy resins are greatly improved with the reinforcing fibers. The ultimate laminates or FRPs can be used in marine industry, aerospace industry, building constriction and electrical insulation [3].

5) **Other applications:** Epoxy resins are also consumed as polymer stabilizers, plasticizers and plastics for pipes.

2.5 **Bio-refinery**

In a bio-refinery, the biomass as a renewable feedstock is refined or converted to high-value products, including green power, biofuels, and bio-based chemicals and materials via various biotechnology, process chemistry and engineering approaches to meet two principal goals: producing sustainable energy and bio-products [21,22].

Figure 2-5 illustrates an overview of production of transportation fuels such as ethanol, gasoline, and diesel fuel from the lignocellulosic biomass [23]. It can be observed that liquid fuels can be obtained from biomass based on three district strategies, including synthesis gas (syn-gas) production and conversion via gasification [24], bio-oil production by pyrolysis [25,26] or liquefaction [27], and hydrolysis of biomass to produce sugar monomer units [23]. Fischer-Tropsch (F-T) synthesis is an important process to utilize syn-gas for producing hydrocarbon fuels in the presence of nickel and cobalt-based catalysts [24]. Syn-gas can also be converted to methanol by catalytic conversion process with Cu/ZnO based catalysts, and to hydrogen via water-gas shift reaction (WGS) catalyzed by nickel-based catalysts. Bio-oils are not regarded as an
appropriate replacement of transportation fuels due to their poor volatility, high viscosity, high water content, low heating value, corrosiveness, high oxygen content and low chemical stability over time and temperature [23,28]. Therefore, bio-oils must be upgraded by catalytic processes such as hydrodeoxygenation (HDO) or catalytic cracking over zeolite to generate high grade oil product [28,29]. Sugars can be converted to valuable fuels through fermentation [30], catalytic dehydration [31], and aqueous-phase processing using heterogeneous catalysts [32].

![Figure 2-5](image-url) Overview of production of fuels from lignocellulosic biomass, reprinted with permission from ref. [23]. Copyright (2006) American Chemical Society.

Beside the bio-fuels production, high-value bio-based chemicals can also be the products of bio-refinery. Figure 2-6 gives an example on producing bio-based chemicals (chemicals and polymers) from lignocellulosic biomass via a lignocellulosic feedstock (LCF) bio-refinery. Lignocellulosic materials are made of three precursors:

a) Cellulose, a glucose polymer;

b) Hemicellulloses/polyoses, sugar polymer of predominantly pentoses;
c) Lignin, the phenolic polymer.

Cellulose can be converted into its primary unit (glucose) by enzymatic or acid hydrolysis. Over a fermentation process, value added-chemicals and fuels such as organic acids, solvents and ethanol/butanol can be generated from glucose. Another product of glucose is hydroxymethylfurfural (HMF) which is the precursor material for levulinic acid and a platform chemical for various other high-value chemicals such as 2,5-furandicarboxylic acid (FDCA), 2,5-diformylfuran (DFF), diaminomethylfuran (DAMF) and 5-hydroxy-4-keto-2-pentenoic acid that are intermediates for a variety of synthetic materials. The important product of LCF-bio-refinery of hemicellulose is furfural which is the precursors for synthesis of Nylon 6,6 and Nylon 6. The conversion of lignin leads to generation of the phenolic monomers which can be used as a starting feedstock in synthesis of polymeric materials such as bio-based phenolic resins and a substitute for BPA for epoxy resins as targeted in the present thesis project. This chapter focuses on the production of polymeric materials from lignin.
2.6 Lignin

The wood cell consists mainly of three organic components including cellulose (40-60 wt%), hemicelluloses (25-35 wt%) and lignin (15-30 wt%) (Figure 2-7) [34]. Lignin can be extracted from lignocellulosic biomass by various treatments such as chemical, biochemical and physical processes. The kind of treatment has a significant effect on the ultimate chemical structure, purity and the properties of lignin [35–37]. The extraction process can be classified into two different categories: so-called sulfur processes and sulfur-free processes. Figure 2-8 shows the extraction processes and their corresponding products [35,38]. Currently, the majority of lignin is generated in the kraft pulping processes, and the annual kraft lignin (KL) generation is estimated to be 50 million tonnes, present in the form of “black liquor” that is used mainly in the recovery boilers for heat and power generation in the mills.

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**Figure 2-6** Products of Lignocellulosic feedstock biorefinery, reprinted with permission from ref. [33]. Copyright (2006) Springer.
Lignin is the second most abundant natural renewable polymer after cellulose [39,40] and accounts for between 15 and 30 wt% of wood stem, leading to the rigidity and strength of wood cell walls. Unlike cellulose of a unique well-defined structure, lignin has a three-dimensional network structure and the structure depends on the vegetal species, location, season, etc. [36]. Elucidation of lignin structure plays an important role in its utilization for chemicals and materials. Different analytical methods such as FTIR [41], NMR [42–44] and GPC [45] were applied to explore the structure of lignin.

**Figure 2-7** Schematic structure of wood cells, reprinted with permission from ref [23] with modifications. Copyright (2006) American Chemical Society.
Figure 2-8 Various lignin extraction process and their dominant products [35].

Lignin is a phenolic polymer formed by radical coupling polymerization of three monolignols (Figure 2-9) [45]. The amorphous macromolecular structure of lignin comprises three types of phenyl-propanols, i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, linked together by mainly ether linkages (e.g., \( \alpha-O-4 \), \( 5-O-4 \) and \( \beta-O-4 \)) and condensed linkages (e.g., \( 5-5 \), \( \beta-\beta \), \( \beta-5 \) and \( \beta-1 \) linkages) [46–48] (Fig. 2-10). Around 40% to 60% of total inter-molecular linkages in the structure of lignin are ether bonds and the \( \beta-O-4 \) bond is a predominant ether linkage [45,49]. The dominant monomer in softwood lignins is Guaiacyl (G) monomer, while hardwood lignins consist of both Syringyl (S) and Guaiacyl (G) units [50]. The reactivity of lignin depends on the form and composition of reactive functional groups within monomer units. In particular, lignin mainly contains three types of functional groups: p-hydroxy-phenyl, aliphatic hydroxyl, and carboxylic acid groups [50].
Until recently, lignin has been considered as a waste by-product of paper pulping industry. It is mainly consumed in the mills in recovery boilers for heat and power generation [51], and a small quantity of lignin is used as fillers such as ink varnishes, paints and elastomeric matrices [36]. While in recent decades, there is a growing interest in utilization of lignin as a feedstock for the synthesis of polymeric materials due to the following driving factors [52]:

1) The material is sustainable and renewable,

2) There is immense generation of lignin as a by-product in pulp/paper industry and cellulosic ethanol industry,
3) There are various functional groups present in lignin structure which provide a variety range of chemical reactions,

4) Lignin has intrinsic biodegradability and it is believed that the incorporated polymers with lignin would be more biodegradable than the petroleum based polymers.

Normally, lignin can be used as a filler or can substitute <20-30 wt% of some reactive components in polymers (such as phenols for phenolic resins and polyols for polyurethane, or BPA for epoxy resins, etc.) [36,47,53]. Limited by lignin’s detrimental properties (large $M_w$, poor solubility in organic solvent and low reactivity), a greater substitution ratio of lignin in polymer materials is challenging, but may be achieved by modifications on its structure. Different lignin modification technologies have been explored, which include chemical [54,55], biological [56], photochemical [57,58], and electrochemical [57,59] methods. Among these methods, chemical modification processes have attracted significant interest. It is well known that lignin is a polydisperse natural phenolic polymer, as shown in Figs. 2-9 and 2-10 [39,60,61]. Lignin contains both polar (hydroxyl) groups and nonpolar hydrocarbon and benzene rings, it is thus expected to act as a compatibilizer between hydrophilic natural fibers and a hydrophobic matrix polymer [62]. The presence of the phenolic hydroxyl groups in lignin has also enabled its utilization in the synthesis of various polymers such as phenolic resins [63], epoxy resins [64,65], polyurethanes [52,53,66] and polyesters [66,67].

2.7 Synthesis & Processing of Bio-Based Epoxy Resins

Some studies have been reported on the synthesis of bio-based epoxy resins using wood biomass since 1960s by some Japanese researchers [68]. Various natural resources such as vegetable oils (i.e. soybean oil, linseed oil and palm oil) [68–74], tannins [75–77], rosin [78–80], bark [81], liquefied biomass [82–84] and lignin [85,86] have been used as the precursor in the synthesis of epoxy resin. The main advantage of these kinds of epoxy resins is biodegradation. Among these bio-based epoxy resins, the vegetable oil-based epoxy resins have limited applications in the industry due to the non-aromatic backbone structure, resulting in poor heat endurance, mechanical and other performance properties. Therefore they were used only as plasticizers and modifiers in some industries [68,87–89]. For instance, adding the epoxidized soybean oil to petroleum-based bisphenol A with isophorone diamine system effectively reduced the maximum curing peak
temperature, and promoted the performance of the resulted epoxy resins with respect to water adsorption and chemical resistance [87]. New bio-based epoxy clay nano-composites (organo-montmorillonite clay) were produced with diglycidyl ether of bisphenol F (DGEBF), epoxidized linseed oil (ELO) and methyltetrahydrophthalicanhydride (MTHPA) [65]. These new bio-based nanocomposites exhibited high elastic modulus, glass transition temperature and fracture toughness, thus they might provide potential applications in various industries. A novel bio-based epoxy resin with curable double bonds was developed from itaconic acid [90]. To improve the final properties of the cured resin, divinyl benzene and acrylated epoxidized soybean oil were incorporated in the cured network, and the results demonstrated that its glass transition temperature, tensile strength, flexural strength and flexural modulus were comparable with those of the conventional BPA-based epoxy resins [90]. Dimer acid (the dimer of C18 non-saturation fatty acid) is another bio-based material that was applied to epoxy resins systems. Similar to the vegetable oil based epoxy resins, the dimer acid-based epoxy resin exhibited poor mechanical, electrical properties and heat resistance due to its nonaromatic structure and long side chain [68].

As discussed previously, lignin is a polydisperse natural phenolic polymer, as shown in Figs. 2-9 and 2-10. The presence of the phenolic hydroxyl groups in lignin enables its utilization in the synthesis of various polymers such as phenolic resins [63], epoxy resins [64,65], polyurethanes [52,53,66] and polyesters [66,67]. It is expected that the lignin-based epoxy resin can have properties equivalent to those of the conventional petroleum-based epoxy resins. Lignin-based epoxy resins can be prepared by three different methods [91]:

1) physically blending of petroleum-based epoxy resins with lignin [60,86],

2) pretreatment of lignin to improve lignin’s reactivity followed by epoxidation of the modified lignin with epoxides [92],

3) direct epoxidation of lignin with epoxides [47,93–97].

2.7.1 Physical Blending of Lignin and Epoxy Resin

In the first method, lignin is blended physically with a petroleum-based epoxy resin and curing agent to prepare composite materials. Lignin will react with the epoxy resin upon curing. The
obtained lignin epoxy composites show good compatibility with other materials and good mechanical and dielectric properties after curing at elevated temperatures [60]. In a study, low molecular weight kraft lignin was blended with the 1,3-glycerol diglycidyl ether (an epoxy) and imidazole (a curing agent) for preparation of bio-based epoxy resin [98]. The content of lignin in the composites varied in the range of 20% to 50%, and the best thermoset had the tensile strength and Young’s modulus of 37 MPa and 2.2 GPa, respectively.

In some studies, lignin has been used as a curing agent for epoxy resins. Reinforced green composites were developed by curing DGEBA with lignin (as a curing agent) at a lignin content varying from 15% to 30%, and the effects of lignin content on thermal and mechanical properties of the composites was investigated and compared with the system of the same epoxy resin cured with isophorone diamine. The optimum properties were obtained from a system comprising 25% of lignin [13]. Pan et al. used aminated lignin as a curing agent for epoxy resin [91], here the aminated lignin was synthesized based on a two-step process using alkaline lignin. The alkaline lignin was first dissolved in sodium hydroxide solution, then epichlorohydrine was added and the mixture at 50ºC for 8h to epoxidize lignin. Afterward, the epoxidized lignin was reacted with propane diamine under 80ºC for 4-6 h to prepare the aminated lignin [99]. The aminated lignin was found to be a more reactive cross-linker for epoxy resins owing to its primary and secondary amine groups, and the prepared epoxy resin has uniform and stable structure [91].

However, the limitation of the simple blending approach is that lignin can displace only a small percentage (<20-30 wt%) of epoxy resins. In contrast, the 2nd and 3rd methods would make it possible to completely substitute petroleum-based materials (such as epoxy resins) with lignin-based materials.

2.7.2 Pre-Treatment of Lignin before Epoxidation Reaction

In one study, kraft lignin was reacted first with unsaturated carbonyl groups or unsaturated nitrogen containing compounds to produce alpha- or beta-unsaturated reactive end groups on the lignin molecule. Then, this unsaturated groups were epoxidized by reacting with hydrogen peroxide or sodium peroxide [92].
Several studies were performed on epoxidation of lignin after pretreatment. Sulfuric acid or hydrochloric acid and phenol derivatives were used to cleave the intermolecular bonds of kraft lignin to increase the phenolic hydroxyl groups on the lignin molecules, followed by grafting the lignin molecules by epichlorohydrin under sodium hydroxide condition [68]. To the similar end, ozone oxidation kraft lignin was performed by dissolving the lignin in the dioxane/water mixture followed by oxidation with ozone-containing oxygen. This oxidative treatment could cleave the aromatic ring of lignin and generate muconic acid derivative with carboxyl groups on both ends of the conjugate double bond. The ozonized lignin was then dissolved in alkaline water to crosslink with the water soluble petroleum-based epoxy resins. The crosslinked product has intermolecular penetrating network (IPN) structure with superior adhesion ability on wood substrates [68]. In another modification, alcoholysis lignin was dissolved in ethylene glycol at 80°C and reacted with Succinic anhydride and dimethylbenzylamine for 6 hr. The obtained mixture of ester-carboxylic acid derivatives of alcoholysis lignin and ethylene glycol was reacted with various molar ratio of ethylene glycol diglycidyl ether (EGDGE) at 130°C for 5h to synthesize lignin-based epoxy resin [100,101]. Hofmann et al. [85] prepared epoxy resins from hydroxylalkyl lignin derivatives from organosolv lignin with varying degrees of alkoxylation. In the study of Hofmann et al. [85], hydroxyalkylation of organosolv lignin was conducted by reacting it with propylene oxide to improve the solubility and then with ethylene oxide to convert secondary hydroxyl groups into primary hydroxyl groups, followed by epoxidation of the pre-treated lignin with epichlorohydrin. The epoxidized lignins have an average molecular weight from 1000 to 30000 and the epoxy index from 200 to 700 g/eq. The epoxy-lignin was crosslinked with metaphenylene diamine and then tested for mechanical performance. The epoxy-amine network which contains more than 50% lignin exhibited tensile strengths and moduli in a similar order of the conventional DGEBA-amine networks [85].

Simionescu et al. [102] modified an iron-lignosulfonate by phenolysis reaction with phenol, betanaphthol, bisphenol A and a novolac phenol formaldehyde resin. Then these phenolated products were reacted with epichlorohydrin in alkaline medium (NaOH) at 75°C for 6 hours with different molar ratios of epichlorohydrin. By epoxidation reaction of intermediary phenolated compounds with epichlorohydrin, various proportions of the liquid and solid lignin-epoxy resin fractions were obtained and showed good thermal stabilities. Zhao et al. [96] synthesized epoxy-lignin resins from calcium lignosulfonate. The pretreatment of calcium lignosulfonate was done using sulfuric
acid to convert it into lignosulfonic acid in excess phenol at 95 °C for 3 hours, in order to generate phenolated lignosulfonate. With this modification, the content of phenolic hydroxyl groups was improved and the phenolated lignosulfonate was then epoxidized by epichlorohydrin in the presence of sodium hydroxide as a catalyst. An interesting point of the above epoxy-lignin synthesis method is that two types of epoxy resin (solid phase and liquid phase) were simultaneously produced. The C-NMR spectroscopy analysis evidenced epoxy groups on the structure of liquid epoxy and solid epoxy with new peaks in the range of 80 ppm to 40 ppm [96]. The proposed structure of the solid lignin-epoxy is illustrated in Figure 2-11.

Figure 2-11 The proposed structure of solid lignin-epoxy resin, Reprinted with permission from ref [96]. Copyright (2001) Springer.

Huo et al.[103] synthesized a lignin and cardanol based novolac epoxy resin (LCNE). Cardanol was treated with sulfuric acid for 3h at 150ºC, cooled to 90ºC and reacted with lignin, hydrochloric acid and the water solution of formaldehyde for 3h. The obtained product was neutralized by NaOH solution and dried, followed by reacting with epichlorohydrin in the presence of
benzyltriethylammonium chloride (BTEAC) at 70°C for 4h. NaOH solution in 8 times of stoichiometric amount was added and allowed for 4 hours reaction at a fixed temperature. Finally, the viscous LCNE was produced. Figure 2-12 shows the possible structure of LC-novolac epoxy resins.

![Figure 2-12 Schematic structure of lignin-cardanol- novolac epoxy resin, reprinted with permission from ref [105]. Copyright (2014) Elsevier.](image)

2.7.3 Direct Epoxidation of Lignin

As reported by Simionescu et al. [64], calcium lignosulfonate was reacted directly with epichlorohydrin under alkaline conditions at 70-75°C for 4.5- 7.5 h and various compositions of sodium hydroxide and various molar ratios of epichlorohydrin (ranging from 100 g-212 g). The use of high concentrated sodium hydroxide and low molar ratio of epichlorohydrin led to a prepolymer with high viscosity and high epoxy equivalent. Although the curing of the lignin-based epoxy resin with diaminodiphenyl methane was slower than that of conventional petroleum-based epoxy systems, the shear strengths of bio-based epoxy films were found to be comparable to those of the conventional epoxy resin films. Hirose et al. [94] synthesized epoxy prepolymer from alcoholyis lignin and lignin-related phenol such as p-hydroquinone (HQ) and methoxy-p-
hydroquinone (MHQ) via reaction with epichlorohydrin in a NaOH aqueous solution at 100 °C for 5 h. The synthesized epoxy resins were cured with poly-(azelaic anhydride). Delmas et al. [47] used lignin as a substitute for bisphenol-A in synthesis of epoxy resin. The epoxidation reaction was carried out by dispersion of lignin in water in the presence of an Ultra-Turrax T18 disperser (IKA, Staufen, Germany). Then, the pH of the system was adjusted into around 12 with aqueous NaOH. At last, poly (ethyleneglycol) diglycidyl ether (PEGDGE) was added as an epoxide agent and the mixture was heated up to 60ºC and kept at this temperature for 2 h. The chemical structure of lignin-based epoxy resin was analyzed by solid state 13C NMR. In another research, glycidyl etherification of liquefied wood was achieved with 10 molar ratio of epichlorohydrin and 2 fold of sodium hydroxide at 100°C for 2.5 hours [82,84].

Malution et al. [97] modified lignin via hydroxymethylation (reaction with formaldehyde in alkaline medium) prior to epoxidation. The epoxidation process was done on both unmodified lignin and hydroxymethylated lignin. Effects of reaction parameters, e.g., reaction temperature, reaction time, epichlorohydrin/lignin molar ratio and NaOH/lignin molar ratio. The results indicated that increasing temperature and reaction time had a negative effect on the epoxy index of product due to crosslinking reactions. Also the modified lignin (hydroxymethylated lignin) derived epoxy resins had a lower epoxy index in comparison to that of the one derived from unmodified lignin. Masouri et al. [95] epoxidized kraft lignin to improve its application potential. Before epoxidation, two different treatments were performed on the kraft lignin. The first treatment was methylolation of kraft lignin via reaction with formaldehyde and the second one was glyoxalation of kraft lignin by glyoxal. Epoxidation was then carried out on unmodified kraft lignin (KL), methylolated kraft lignin (MKL) and glyoxalated kraft lignin (GKL). H-NMR results indicated that the MKL has more aliphatic hydroxyl groups than KL and GKL. Hence, the methylolated lignin with higher content of hydroxyl group could be resinified to form more useful materials, especially epoxy resins. Their results suggested that the best condition for the synthesis lignin-based epoxy resin is 70°C for 3 h in the presence of 1/3 lignin/NaOH ratio (w/w). If the value of each of these parameters increased, the epoxy index could decrease due to the possibility of secondary reaction occurring between the formed epoxy groups and the free phenolic hydroxyl groups. Epoxy resins from the epoxidized methylolated kraft lignin and the epoxidized glyoxalated kraft lignin have a higher value of epoxy index in comparison with the epoxidized unmodified kraft lignin because of their higher contents of aliphatic hydroxyl groups in both lignin samples.
Sasaki et al. used steam-explored bamboo lignin as a replacement for bisphenol A in synthesis of epoxy resins [104]. The epoxidation reaction is based on a two-step reaction. Initially, bamboo lignin reacted with epichlorohydrin in presence of a phase transfer catalysis using tetrabutylammonium bromide (TBAB) at 80°C for 4h under nitrogen. It is an addition reaction leading to opening the epoxy ring. In the second step, the aqueous NaOH and 5ml of dimethylsulfoxide were added and the final mixture was stirred for 12 h at 10°C. In the second step of the reaction, HCl is removed from the resin precursors and the epoxy ring is reconstructed. In another research, a methanol soluble lignin was reacted with epichlorohydrin in alkaline condition for 3h at 110°C [83]. Similarly, Singh et al.[105] synthesized bio-based epoxy resin by directly reacting lignin and epichlorohydrin in the ratio of 2:3 (w/v) in alkaline condition at 80°C for three hours reaction. The synthesized lignin-based epoxy was blended with a conventional epoxy primer in different weight % from 5 wt% to 20 wt%. 5 wt% of epoxidized lignin in the primer increased the pot life of the paint, but the pot life was reduced if further increasing the content of epoxidized lignin in the primer, and increasing the lignin-based epoxy resin in formulation increased the corrosion rate of the paint.

2.8 Curing Kinetics Study

The ultimate properties of an epoxy resin depend on both its chemical composition and the curing process [106,107]. Therefore, it is essential to investigate the curing process of epoxy resin and the cross-linked structure of the resin. In comparison with thermoplastics, processing of thermosets composites is more complicated and less controllable because in processing of a thermoset composite, polymer synthesis and shaping occur at the same time. During the curing process of fiber reinforced composites, two major physical transformations of the corresponding thermoset polymers, i.e., gelation and vitrification, take place [108]. The mechanism and kinetics of the thermoset polymer curing determine the network morphology, which in turn, dictates the physical and mechanical properties of the cured products [109].

The curing process can be monitored by different techniques such as DSC, dynamic torsional vibration method (DTVM) [110–112], FTIR [113], rheokinetic measurements [114], dielectric measurements [115,116], etc.
Curing kinetics of lignin-based epoxy resins have been also studied in the literature. For instance, Sun et al. investigated curing kinetics of a liquid lignin-based epoxy resin (LEPL) cured with three different curing agents including methylhexahydrophthalic anhydride (MTHPA), maleic anhydride (MA) and 2-methyl-4-methylimidazole (EMI-2,4) [106,107]. The kinetic parameters were evaluated based on Kissinger method and autocatalytic kinetics. The apparent activation energy calculated from Kissinger method for the cured resin system with the curing agent of MTHPA, MA and EMI-2,4 is 76.54, 56.35 and 47.22 kJ/mol, respectively. The curing kinetic of LEPL-MTHPA followed approx. first order model, while the two others systems had autocatalytic kinetics with overall order of 1.47 for LEPL-MA and 1.15 for LEPL-EMI-2,4 system. Hirose et al. [14] synthesized epoxy resins with polyester chains derived from biomass components such as saccharides, lignin and glycerol. The activation energy was determined to be around 83.5 kJ/mol when the extent of curing was below 60%, and it increased to 110 kJ/mol at higher curing extent >80%, likely due to a reduced diffusion rate.

The curing kinetics of lignin-cardanol based novolac epoxy resin with methyl tetrahydrophthalic anhydride (MeTHPA) was studied by DSC and evaluated by Friedman method and Malek Method [103]. Different from what described above, the activation energy increased with the curing extent up to 50% extent, but remained constant approx. 52 kJ/mol up to the completion of the curing process. The reaction of epoxy group and anhydride can be catalyzed in the presence of tertiary amine. The tertiary amine reacts with anhydride groups to generate a zwitterion. The carbonyl anion on the zwitterion quickly reacts with the epoxy group to form a new alkoxide anion that can attack the anhydride to form new Zwitterions. The above propagation mechanism for epoxy resin curing may account for the increased activation energy at its initial curing stage, and the constant activation energy at a higher curing extent.

Curing kinetics of lignin blended by epoxy resin were studied by Kong et al. [15], where a polyblended lignin-epoxy resins as adhesives were prepared with a hydrolyzed lignin. The bonding properties and curing kinetics of the prepared adhesives were investigated. Introducing lignin into the epoxy resins could promote the curing reaction and improve the shear strength. Yin et al. [117] studied the mechanical properties and curing reaction of an epoxy resin blended with enzymatic hydrolysis lignin from cornstalk. The hydroxyl and carboxyl groups of lignin could react with
epoxy groups, and lignin’s polyphenol structure could catalyze the epoxy curing reaction. An epoxy resin blended with carboxylic acid functionalized alkali lignin (AL-COOH) at three blending levels: 0.5, 1 and 2%, was cured by anhydride [118]. The results revealed that AL-COOH did not change the mechanism of the curing reaction as the main exothermic peak remains constant for all samples, while a new exothermic peak appeared in the range of 130-140ºC which can be attributed to the reactions between the epoxy groups and carboxyl groups on AL-COOH.

2.9 Mechanical Properties of Lignin-Based Epoxy Resins

The final performance of epoxy resins depends on the chemical composition and the curing process. In particular, the curing of epoxy resin is very important as it provides a way to control its manufacturing process to minimize the internal stress and to produce a high performance finished product [119–121]. On the other hand, the introduction of lignin into an epoxy resin changes the chemistry of epoxy resin, and hence would change the mechanical properties of the epoxy resin.

Lignin-based epoxy resins were synthesized and tested for mechanical and adhesion properties by Kishi et al. [82,84]. The prepared lignin-based epoxy resins were cured with diaminodiphenyl sulphone (DDS) and diaminodiphenyl methane (DDM), separately. The bio-based epoxy resins exhibited a lower glass transition temperature in comparison with a conventional BPA-based epoxy resin. The lignin-based epoxy/DDS system showed higher storage modulus of elasticity at room temperature and higher flexural modulus of elasticity as well as higher flexural strength, in comparison with the petroleum-based epoxy resin. However, the storage modulus of elasticity of the lignin-based epoxy/DDM sample was similar to that of the conventional BPA-based epoxy resin.

Polyblending an epoxy resin and a lignin increased the mechanical properties of the resin owing to an increased cross-linking density, caused by the reaction between epoxy groups and the hydroxyl and carboxyl functional groups [15].

An interesting study was reported by Liu et al. [118] on using a modified alkali lignin as a toughening agent in epoxy resin. Alkali lignin was treated by anhydride hardener in different ratios (0.5, 1 and 2%) to form a carboxylic acid-functionalized lignin, which improves the miscibility of the lignin in epoxy matrix. Then, the modified lignin was blended with the conventional BPA-
based epoxy resin at 0.5 wt.% to 2 wt.% blending ratio. Figure 2-13 shows the proposed structure of lignin-epoxy system.

\[ \text{Figure 2-13} \] Schematic display of the epoxy-lignin network, reprinted with permission from ref \[118\]. Copyright (2014) American Chemical Society

Komiya et al. [18] studied the mechanical (by DMA) and dielectric properties of cured DGEBA epoxy resins with soda lignin (SLG) and methanol extracted SLG (me-SLG). The DMA results showed that both samples have one glass transition temperature, suggesting that the epoxy resins cured with lignin derivatives have a homogeneous structure. Me-SLG has lower molecular weight and more reactive hydroxyl groups in comparison with SLG. Hence, the initial viscosity of DGEBA-me-SLG was lower than the DGEBA-SLG. Furthermore, the $T_g$ and flexural strength of DGEBA-me-SLG were higher than DGEBA-SLG. Feldman [122] investigated effects of different types of lignin on the adhesion properties of epoxy resin. It was reported that the hardwood lignin enhanced the adhesion of epoxy resin more than the softwood lignin (Indulin). Adding 20% tomlinite lignin (hardwood lignin) to an epoxy resin provided the highest adhesive joint shear strength for the epoxy resin. It was concluded that the kind and content of functional groups of the lignin added and its molecular weight are the main factors that influence the final performance of an epoxy resin. However, in another work, kraft lignin was blended with a liquid epoxy resin and a curing agent up to 20 wt.% [123]. When the lignin loading content is below 20 wt%, the cured
samples showed one glass transition temperature, suggesting that the epoxy resins cured with a small loading of lignin (<20 wt%) have a homogeneous structure. However, two $T_g$s were observed if increasing the content of lignin to 20 wt% or higher.

### 2.10 Thermal Properties of Lignin-Based Epoxy Resins

Thermal stability of polymeric materials plays an important role in their final applications. Thermal stability of a polymeric material can be characterized by thermogravimetric analysis (TGA) measuring the weight loss of the sample as a function of temperature or time.

Generally, introduction of lignin into a polymeric matrix could promote the thermal stability due to the aromatic structure of lignin and lots of polar bonds on the structure of lignin [91,124–127]. Lignin was considered as a thermal stabilizer for cellulose against thermal oxidation at low temperature due to its tendency of radical scavenging [128]. Thermal stability of extracted lignin from sal (shorea robusta) leaves was evaluated by TGA, and the first weight loss peak happened at around 110ºC which is believed associated to the moisture loss and the second peak was detected at around 440ºC which can be corresponding to the start of thermal degradation [105]. Thermal decomposition of lignin-brominated epoxy flame retardant system was analyzed by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and thermogravometry/mass spectrometry (TG/MS) [128]. It was realized that the brominated epoxy with lignin shifted the decomposition temperature into higher temperature and the generation of bromomethane increased because of the propensity of radical scavenging of lignin. The thermal stability of lignin can be improved by the acetylation of hydroxyl groups on the structure of lignin, as evidenced by the results from the literature work [14], which demonstrated that thermal decomposition temperature of a lignin shifted from 230ºC to 289ºC after modification of the lignin via acetylation. Literature also shows that the thermal stability of lignin depends on its plant source, the extraction process and the operating parameters such as reaction temperature, pressure, heating rate and degradation atmosphere [105,129,130]. Typical decomposition of a lignin shows the first mass-loss peak in the range of 100-180ºC due to elimination of humidity, the second mass-loss peak at 280-390ºC and the third peak at around 420 ºC [129]. Therefore, upon being heated lignin decomposes slowly and in the broad range of temperature leading to a char yield of around 45% [131]. In order to determine the kinetics parameters of thermal decomposition of lignin, the distributed activation energy model (DAEM) has been used in several studies [130,132].
Thermal stability of lignin-based epoxy resins has also been studied and the results are summarized as follows:

Thermal properties of epoxy resin cured by different combination of aminated lignin and W39 amine curing agent demonstrated that with increasing the content of aminated lignin from 20% to 100% the temperature at 10% mass loss (T\textsubscript{10}) increased to higher temperature, suggesting improved thermal stability by lignin addition [91]. Petreus et al. [133] synthesized a new phosphorus containing lignin-based epoxy resin from aspen wood lignin. The lignin reacted with epichlorohydrin in the presence of NaOH as a catalyst. The prepared prepolymer was cured with [2-(6 oxide-6H- dibenz(c,e)(1,2)oxaphorin-6-yl)]-1,4naphtalendiol (NBQ) and characterized for the chemical structure of the lignin-based epoxy before and after curing by FTIR spectra. Thermal properties of the lignin-based epoxy before and after curing were investigated by TGA and indicated that the phosphorus modified lignin-based epoxy has higher thermal stability. On the other hand, Sasaki et al. [104] reported different results from their studies on the thermal stability of cured bamboo lignin-epoxy resin (BL-epoxy) with two different curing agents, i.e., bamboo lignin (BL) and 1-(2-cyanoethyl)-2-ethyl-4-methylimidazole (2E4MZ-CN). It was observed that both the BL-epoxy resin cured by BL and the BL-epoxy resin cured by 2E4MZ-CN had a lower decomposition temperature compared to the conventional BPA-based epoxy (DGEBA) cured by 2E4MZ-CN. However, the thermal stability of bio-based epoxy systems can meet the minimum requirements for being used as solder-dip resistance (250-280ºC) in printed circuit boards.

2.11 Summary of the Literature Work

1. As the production of epoxy resin has long relied upon petroleum resources, it is imperative to find an appropriate substitute for future manufacture of epoxy resins.
2. Lignin and its derivatives are promising sources of bio-phenol in synthesis of epoxy resin.
3. Modification of lignin prior the epoxidation reaction can promote the reactivity of lignin toward epichlorohydrin.
4. De-polymerization of lignin may be effective for generation a reactive feedstock for synthesis of bio-based epoxy resins.
5. Introduction of lignin into a polymeric matrix could promote the thermal stability and mechanical performance of the ultimate product.
6. The curing kinetics of lignin-based epoxy systems needs to be precisely evaluated using DSC to determine the mechanism of curing process.

7. The industrial applications of lignin-based epoxy resin needs to be demonstrated in future work.
2.12 References


Chapter 3

Chemically Modified Lignin through Epoxidation and its Thermal Properties
Abstract

Chemical modification of lignin could improve the lignin’s performance as a biopolymer and offer new fields of application of lignin to biomaterials. In the present work, a novel chemical modification process was developed to modify a reductively degraded organosolv lignin by epoxidation - grafting an epoxide group onto lignin. The chemical structure of the resulting lignin-based epoxy resin was characterized with FTIR to confirm the presence of epoxied groups on the lignin structure and also the reduction of hydroxyl groups compared with the original lignin sample before grafting. To optimize the process and to achieve the optimal number of epoxy groups on the lignin structure, the effects of reaction time, reaction temperature and epichlorohydrin/lignin molar ratio were investigated. The as-prepared lignin-based epoxy samples were characterized using gel permeation chromatography (GPC) for their molecular weights and distribution, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) for their thermal properties.
3.1 Introduction

The increasing need for environmental protection together with concerns about the future availability of petrochemical feedstock have led to the design and development of new bio-based chemicals and materials using renewable resources [1]. Lignin is the second most abundant natural renewable polymer after cellulose [2, 3]. Lignin is an amorphous macromolecule comprised of three phenyl-propanols i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, linked together by condensed linkages (e.g., 5-5, β-β, β-5and β-1 linkages) and ether linkages (e.g., α-O-4, 5-O-4 and β-O-4) [4-6], and contains polar (hydroxyl) groups and nonpolar hydrocarbon and benzene rings. The lignin content in woody stem varies between 15%-40%. Lignin is considered a by-product of paper pulping and is viewed as a waste product (annual generation is estimated at 50 million tons worldwide); it is often used as a fuel to improve the energy balance of the pulping process. The annual sales of lignin as specialty chemicals account for a mere 1% of total lignin produced from various sources[2]. The availability and functionality of lignin provide the possibility of using it as a derivative phenolic feedstock to synthesize various polymers.

Epoxy resins are highly versatile materials due to their excellent properties such as superior chemical resistance, superior moisture and solvent resistances, good thermal and dimensional stabilities, high adhesion strength, and superior electrical properties. These properties provide diverse applications for epoxy resins in the fields of high-performance composites, industrial coatings, adhesives, electrical-electronic laminates, flooring, and paving applications [7, 8].

Previous research has shown that lignin can be modified by grafting to produce lignin-based epoxy resins as biomaterials or adhesives. The synthesis of lignin-based epoxy resins can be divided into three categories: (a) physical blending of epoxy resins with lignin [9, 10]; (b) directly modifying lignin using epoxides [5, 11-15]; and (c) Two-step processes involving the generation of chemically modified lignin with improved reactivity and the subsequent reaction of these products with epoxides [16]. In most studies, the epoxidation reaction of lignin was carried out in the presence of off-stoichiometric molar ratios of epichlorohydrin (10 times) and sodium hydroxide (3 times) in an aqueous medium. This synthetic method presents some challenges; for example, a large quantity of epichlorohydrin was used without any investigation of its unreacted amount.
Furthermore, there has been no extensive study on a de-polymerized lignin to produce an epoxidized lignin.

The new materials targeted here are lignin-based epoxy resins for adhesives and coating materials. Based on the Global Industry Analysts (GIA) announcement, the global market for epoxy resins will reach 3.03 million tons by 2017. The common epoxy resin is derived from petrochemical feedstock, and there are concerns about the sustainability of this non-renewable petroleum resource. The main goal of this project is to develop a bio-based epoxy resin with satisfactory properties to replace petroleum-based epoxy resin for adhesives and coatings. This work is a preliminary study which aims to synthesize lignin-based epoxy resins with a low amount of epichlorohydrin. Further work on the properties and applications of the lignin-based epoxy resins obtained from this research will be reported in the future.

3.2 Experimental

3.2.1 Materials

The materials used in this investigation were organosolv lignin (OL, hardwood), epichlorohydrin, sodium hydroxide, and ruthenium 5% wt on carbon (Ru/C) as a catalyst. The organosolv lignin was provided from Lignol. Epichlorohydrin, sodium hydroxide, and Ru/C were obtained from Aldrich and Caledon. These materials were used as received.

3.2.2 De-polymerization of Organosolv Lignin

The de-polymerization process for organosolv lignin was carried out in a 500ml Parr stirred autoclave reactor. In this process, 50 g organosolv lignin, 2 gr Ru/C (as a catalyst), and 150 g of acetone were loaded into the reactor. The reactor was closed and evacuated and purged twice with N₂ to ensure complete removal of any air or oxygen present within the enclosed reactor. The reactor was then pressurized with H₂ to 100 bar, and the leak test was performed. The reactor was then heated up under stirring to 350°C. After a one-hour reaction at 350°C, the reactor was immediately quenched with water to stop further reaction. The gaseous product was analyzed by GC-TCD and found to be composed mainly of H₂, CH₄, CO₂, C₂H₆, and C₃H₈. The liquid product was transferred to a previously weighed flask. Acetone was removed in a vacuum rotary evaporator at 50°C. The yield of the de-polymerized lignin was 85 (±2) %.
3.2.3 Epoxidation of De-Polymerized Lignin

The epoxidation of de-polymerized organosolv lignin was conducted under alkaline conditions. Various factors that may influence the properties of lignin-based epoxy resin were investigated, including reaction time (3 and 5 hours), reaction temperature (50°C, 70°C and 90°C) and epichlorohydrin/lignin molar ratio (E/L =1, 2, 4 and 10, the average molecular weight of monomers of lignin is 180g/mol). In the epoxidation process, the required amounts of epichlorohydrin and water were loaded into a three-neck glass reactor (250 mL) and heated in an oil bath to reach the required temperatures. Then the previously mixed alkaline lignin solution was added slowly to the reactor for 15 min and allowed to react over a pre-specified reaction time. Afterwards, the solid lignin-based epoxy resin was separated by filtration, and washed several times with distilled water, and then dried at 30°C under vacuum for 6 hours and weighted to determine the yields of solid lignin-based epoxy resins. The sample names illustrate all reaction conditions as showed in Figure 3-1.

![Sample Name: 1E 1.5N 3H W 70](image)

**Figure 3-1** Sample names.

3.2.4 Analytical Methods

The lignin-based epoxy resin was analyzed by Fourier Transform Infrared Spectroscopy (FTIR) to prove the presence of epoxy groups. The average molecular weight and polydispersity index (PDI) of the synthesized lignin-based epoxy resin were determined using a Waters Breeze GPC-HPLC instrument (1525 binary lamp, UV detector set at 270 nm, Waters Styragel HR1 column at 40°C) using THF as the eluent at a flow rate of 1 ml/min with linear polystyrene standards for building the molecular-weight calibration curve. The thermal analysis of lignin-based epoxy resins
was studied by thermal gravimetric analysis (TGA) (TA instrument, Model Q50, heating rate: 10°C/min from 30-700°C under a nitrogen flow of 50 ml/min) and Differential Scanning Calorimetry (DSC) (TA instrument, Model Q10, heating rate: 10°C/min from 30-350°C under nitrogen purge at 50 ml/min).

3.2.5 Results & Discussions

FTIR spectroscopy was used to characterize the raw materials and to analyze changes in the lignin structure after the modification reactions. Figure 3-2 shows the FTIR spectra of the original, de-polymerized, and epoxidized de-polymerized lignin samples. The spectra of the epoxidized de-polymerized organosolv lignins were almost identical, and for this reason, only some of them are presented for comparison. The spectra of all samples have a broad absorption between 3200-3550 cm\(^{-1}\), which can be attributed to O-H stretch vibration of both aliphatic and aromatic O-H bond stretching from phenolics as well as to the moisture inevitably contained in samples. The peak at 1720 cm\(^{-1}\) corresponds to carbonyl groups in lignin [13]. The peak at 956 cm\(^{-1}\) in the spectra represents vibration of epoxy groups [15], which indicates the presence of epoxy functionality in the epoxidized de-polymerized organosolv lignins. This peak is very sharp in samples with a high epichlorohydrin/lignin molar ratio (4 and 10) and appears as a shoulder in those with a low E/L ratio (1 and 2). This result might be due to occurring of homopolymerization reactions (reactions between epoxy groups and hydroxyl groups on lignin) at low E/L ratios. In contrast, at higher E/L ratios, excess amounts of epichlorohydrin are present, which limit the homopolymerization reactions [17].
One of the effective parameters that affect the applicable properties of epoxy resins is the molar ratio of E/L in the epoxidation process. Therefore, different molar ratios were selected in this research for epoxidation of the de-polymerized lignin. The results clearly indicated that with increasing E/L molar ratio from 1 to 10, the product changed in appearance from a yellowish powder to a dark brown sticky material. The effects of other factors on the physical state of the lignin-based epoxy resins were found to be less significant. The effects of E/L molar ratio on the yield, average molecular weight, and polydispersity index of solid products were also evaluated.

Figure 3-2 FTIR spectra of original, de-polymerized and epoxidized organosolv lignins.
Yields of lignin-based epoxy samples were calculated based on the dried de-polymerized lignin used in the epoxidation process and are shown in Figure 3-3. The main trend illustrates that with increasing E/L molar ratio, the solid yield of epoxidation process increased from 86.7 % to 107.36 % for a three-hour reaction and from 93.8 % to 126% for a five-hour reaction.

The inverse effect of E/L molar ratio was observed on average molecular weight, i.e., a higher E/L led to a lower $M_n$ or $M_w$ (as shown in Table 3-1). The samples synthesized with E/L = 1.0 could not be analyze by GPC because they are not soluble in THF or other common solvents. The average molecular weight and polydispersity index (PDI) of the original organosolv lignin were 2638 g/mol ($M_w$) and 3.58, respectively. After de-polymerization, the $M_w$ decreased to 760 g/mol with a narrower PDI of approximately 2.0. After epoxidation, the average molecular weights of the synthesized samples increased dramatically, which indicates the attachment of several lignin molecules alongside the epoxidation reaction. With increasing E/L molar ratio from 2 to 10, the $M_w$ decreases from 7476 g/mol to 3470 g/mol and from 7037 g/mol to 3386 g/mol for a three- and five- hour reaction, respectively. These results are in good agreement with results reported for the synthesis of common epoxy resins [17, 18]. Also increasing the E/L molar ratio from 2 to 10 had a positive effect on narrowing the polydispersity index of the lignin-based epoxy resins. Samples that were produced with E/L ratios of 2 and 4 showed two peaks in the GPC corresponding to higher-molecular-weight components that might result from cross-linking reactions [19]. However, this phenomena was not observed for samples synthesized with an E/L of 10. An excess
of epichlorohydrin in the reaction system would increase the probability of reaction between phenolates and epichlorohydrin and prevent the homo-polymerization of the products [20].

Table 3-1 Effect of E/L molar ratio on average molecular weight and polydispersity index.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>UV</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
<td>Mw</td>
<td>PDI</td>
</tr>
<tr>
<td>Original lignin</td>
<td>735</td>
<td>2638</td>
<td>3.58</td>
</tr>
<tr>
<td>Degraded lignin</td>
<td>370</td>
<td>760</td>
<td>2.0</td>
</tr>
<tr>
<td>2E1.5N3HW70</td>
<td>1043</td>
<td>7476</td>
<td>7.16</td>
</tr>
<tr>
<td>4E1.5N3HW70</td>
<td>779</td>
<td>3469</td>
<td>4.45</td>
</tr>
<tr>
<td>10E1.5N3HW70</td>
<td>766</td>
<td>3470</td>
<td>4.53</td>
</tr>
<tr>
<td>2E1.5N5HW70</td>
<td>1021</td>
<td>7037</td>
<td>4.65</td>
</tr>
<tr>
<td>4E1.5N5HW70</td>
<td>854</td>
<td>3863</td>
<td>4.52</td>
</tr>
<tr>
<td>10E1.5N5HW70</td>
<td>834</td>
<td>3386</td>
<td>4.06</td>
</tr>
</tbody>
</table>

Epoxidation processes were carried at various temperatures and for various times at E/L molar ratios of 2 and 4, and the product yields are shown in Figure 3-4. Generally, epoxidation with an E/L of 2 led to a lower product yield. Effects of reaction temperature and reaction time on product yields, average molecular weights, and PDI are highly complex, depending on the E/L ratio. For instance, at E/L = 2, the best condition is 3 h reaction at 90°C to achieve the highest yield (approx. 108%) of lignin-based epoxy resin (M_w = 5383 g/mol and PDI=5.22). On the other hand, at E/L = 4, the optimal conditions for the epoxidation process are 5 h reaction at 70°C for the highest yield (approx. 110%) of lignin-based epoxy resin (M_w = 3863 g/mol and PDI=4.52).
The other proof of success in grafting epoxy groups to lignin structure is thermal behavior. The thermal behaviors of the original organosolv lignin, de-polymerized lignin, and epoxidized lignins are compared in Figure 3-5 (TGA plots) and 3-6 (DSC plots). The solid lignin-based epoxy resins exhibit a higher thermal stability than the de-polymerized lignin, which can be attributed to cross-linkings induced by epoxy groups. The original and de-polymerized lignins show only one event of weight loss on their TGA plots, and their DSC curves do not show any exothermic peak (no chemical reactions between hydroxyl/carbonyl groups to release volatile compounds) in the range of 30 °C -700 °C, which confirms thermal degradation only for these lignins upon heating. However, epoxidized lignin samples (at E/L >=2) showed two events of weight loss in the TGA measurement. The first mass loss peak was observed at 200 °C -300 °C, at which an exothermic peak was also observed in the DSC measurement of the same material. This mass loss might be attributed to cross-linking (or self-curing) of the epoxidized sample (the reaction between epoxy groups and hydroxyl groups) [21]. The second mass loss peak at a higher temperature (>350 °C) might be due to thermal degradation of epoxidized lignin materials.

Figure 3-4 Effects of reaction temperature and reaction time on product yield.
### Figure 3-5 TGA plots of original, de-polymerized and epoxidized lignins.

### Figure 3-6 DSC curves of original, de-polymerized and epoxidized lignins.

#### 3.3 Conclusions

This study is different from other research work on epoxidized lignins, where the original lignin was used as a feedstock for the epoxidation process and the synthesized epoxy products had high average molecular weights which are not appropriate for epoxy resin applications. In the present study, the molecular weight of the original lignin was reduced through a de-polymerization process, and a bio-based epoxy resin was produced with suitable average molecular weight and
distribution for applications. In this work, organosolv lignin was de-polymerized in the presence of hydrogen and then modified by epoxidation. The epoxidation process was conducted under various conditions to investigate the factors affecting product yields and properties. The grafting of epoxy groups onto the lignin structure was evidenced directly by FTIR spectroscopy. By increasing the molar ratio of E/L, the product yield generally increased, and the molecular weight of the lignin-based epoxy resin generally decreased. However, the effects of other factors such as reaction time and reaction temperature on product yield and properties are complex.

For both original lignin and reductively de-polymerized lignin, the TGA measurement showed only one mass loss event in the range of 30 °C–700 °C, and the DSC analysis did not show any exothermic peak in the same temperature range. In contrast, the prepared lignin-based epoxy resins showed two mass loss events in the TGA measurement: the first at around 200 °C–300 °C, and the second above 300 °C, corresponding to homopolymerization (curing) of the lignin-based epoxy sample (as evidenced by the DSC measurement on the same sample) and thermal degradation of the lignin-based epoxy resins, respectively.
3.4 References


Synthesis of Lignin-Based Epoxy Resins: Optimization of Reaction Parameters Using Response Surface Methodology
Abstract

Owing to the presence of phenolic groups in the lignin structure, this provides the potential to substitute bisphenol-A in synthesis of epoxy resin. In this work, organosolv lignin (OL) was first de-polymerized by reductive de-polymerization in supercritical acetone at 350°C in the presence of Ru/C catalyst and 10 MPa H₂. The obtained de-polymerized organosolv lignin (DOL), with a low average molecular weight (M₉) and high hydroxyl number, was used to synthesize lignin-based epoxy pre-polymers. A set of experiments was designed by utilizing the central composite design (CCD) to synthesize lignin-based epoxy resin. Three synthesis variables including reaction temperature, reaction time and NaOH/DOL molar ratio were investigated and the synthesized epoxy pre-polymers were characterized by FTIR and potentiometric titration. The mathematical model derived from the CCD was found to be accurate to predict the optimum conditions. At the optimal synthesis conditions, i.e., 8h at 55°C with NaOH/DOL molar ratio of 6.3, a high product yield (99%) and high epoxy content of ~ 8 were achieved.
4.1 Introduction

Today utilization of renewable biomass resources for biopolymers and bio-chemicals has drawn increasing attention worldwide, due to the serious environmental and resource-depletion issues and concerns related to fossil fuels utilizations [1–3]. Various biomass resources such as lignin [1,4], vegetable oil [5], fatty acid and cellulose [6] were used as a renewable feedstock to synthesize different bio-based polymers including phenolic resin, epoxy resin [2,3,7], polyurethane and polyester [6,8]. Among the renewable resources, lignin may be the best potential candidate for the production of epoxy resin because of its aromatic structure. Lignin is the second most abundant natural renewable polymer after cellulose and accounts for between 15 and 40% of wood stem depending on the type of wood [9]. Lignin is a complex three-dimensional biopolymer of aromatic alcohols. Three monomers, i.e., p-hydroxyl-phenyl propanol (H), guaiacyl-propanol (G) and syringyl-propanol (S) linked together by condensed linkages and ether linkages to generate three-dimensional networks [10,11]. The percentage of these monomers will vary in different kinds of lignin. The dominant monomer in softwood lignins is Guaiacyl (G) monomer, while hardwood lignins consist both Syringyl (S) and Guaiacyl (G) units [12]. The reactivity of lignin depends on the form and composition of reactive functional groups within monomer units. In particular, lignin mainly contains three functional groups: p-hydroxy-phenyl, aliphatic hydroxyl, and carboxylic acid groups [12]. Owing to the presence of phenolic groups in the structure, lignin has the potential to substitute bisphenol-A in synthesis of epoxy resin.

Several studies have been reported on incorporation of lignin in epoxy resin production [1,13–15]. In some studies, lignin was modified before epoxidation reaction to enhance the reactivity of specific functional groups in lignin. El Mansouri et al. [16] synthesized lignin-based epoxy resin by using a raw kraft lignin recovered directly from pulping liquor and two other modified lignin by methylolation and glyoxalation treatments. The $^1$H NMR spectra of these lignins showed that the methylated kraft lignin contained more hydroxyl groups than the glyoxalated kraft lignin. Hofmann and Glasser [17] prepared epoxy resins from hydroxylalkyl lignin derivatives with varying degrees of alkoxylation. The modification was performed via two steps: firstly, reacting lignins with propylene oxide to increase their solubility, and secondly, converting secondary hydroxyl groups into primary ones using ethylene oxide. Delmas et al. [18] used wheat straw-
derived lignin as a resource starting material to synthesize bio-based epoxy resin. Epoxidation reaction was conducted in alkaline aqueous media and polyethyleneglycol diglycidyl ether (PEGDGE) was used as an epoxide agent. The mechanical and thermal properties of the obtained resin were comparable to a petroleum-based epoxy resin. Zhao et al. [19] succeeded to produce bio-based epoxy resin from calcium lignosulfonate. They reported that the solid and liquid lignin based epoxy resins were formed simultaneously and the chemical structure of both products and polymerization mechanism were evaluated by FTIR and NMR. Sasaki et al. [20] used steam-explored bamboo lignin as a feedstock for the production of epoxy resin. The synthesized epoxy resin was cured with a commercial curing agent (1-(2-cyanoethyl)-2-ethyl-4-methlimidazol) or the bamboo lignin. The results showed that the bio-based epoxy resins cured by bamboo lignin provided favorable properties for being used in the electrical industry, but their thermal and mechanical properties need to be improved. In some other studies, pretreatment on lignin was performed with acid and phenol derivatives to cleave the lignin intermolecular linkages and hence increase the functionality of phenolic hydroxyl group in the structure of lignin [1,21,22].

Although the epoxidation of various types of lignin have been documented, no report is currently available on the epoxidation of de-polymerized lignin and investigating the process parameters on epoxidation reaction. The objective of this work is to de-polymerize organosolv lignin to produce a more reactive feedstock to synthesize epoxy resins, and to screen the important process parameters in order to maximize the yield and the epoxy content of the synthesized epoxy pre-polymers. Three most important factors for epoxidation reaction including reaction temperature, reaction time and NaOH/DOL molar ratio were used in the screening experiments.

4.2 Response Surface Method (RSM)

Response surface methodology, RSM, was introduced in the early 1950s. RMS is a collection of mathematical and statistical techniques which explore the effects of several variables on one or more responses. The aim of the RSM analysis is to optimize the responses [23,24]. The relationships between the response and variables can be a simple polynomial or be a complex system described by nonlinear functions such as exponential function or Lagrange’s interpolations [24].
Central Composite Design (CCD) is one of the most commonly used RSM designs using a quadratic fitting model (second-order model) to predict and optimize the responses. The quadratic equation can be presented by following equation [24].

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j + \varepsilon \] (4-1)

where \( Y \) is the response, \( \beta_0, \beta_i, \beta_{ii} \) and \( \beta_{ij} \) are the regression coefficients for the intercept, linear, quadratic and interaction parameters, respectively, \( X_i \) and \( X_j \) are the independent variables and \( \varepsilon \) represents the noise or error component observed in the response [24,25].

### 4.3 Methods

#### 4.3.1 Materials

Organosolv lignin (OL, hardwood) used in this study was supplied by Lignol. It is a dark brown powder with an average molecular weight is \( \approx 2600 \) g/mol (PDI \( \approx 3.6 \)) based on our GPC analysis. Other chemicals used in this study included ruthenium 5% wt. on carbon (Ru/C) as the catalyst for lignin de-polymerization, acetone, epichlorohydrin (ECH), tetrabutylammonium bromide (TBAB), sodium hydroxide, \( d \)-chloroform, tetrahydrofuran (THF, HPLC grade), pyridine, acetic anhydride and dibromomethane. All chemicals were purchased from Sigma-Aldrich and used without any further purification.

#### 4.3.2 De-polymerization of Organosolv Lignin

Organosolv lignin (OL) was de-polymerized according to the methods as described in details in our previous paper [26]. Briefly, 50 g OL, 150g acetone and 2 g Ru/C as a catalyst were loaded into a 500 ml Parr stirred autoclave reactor. The reactor was purged with nitrogen twice to assure the complete removal of oxygen and air from the reactor. Then, the reactor was pressurized with 100 bar \( \text{H}_2 \). The reactor was heated to 350\(^\circ\)C for 1 h reaction. Then the reactor was quenched to room temperature to stop further reactions. The gaseous phase was collected with a gas bag and analyzed with GC-TCD. The gaseous phase mainly contained \( \text{H}_2, \text{CH}_4, \text{CO}_2, \text{C}_3\text{H}_8 \) and \( \text{C}_2\text{H}_6 \). The liquid phase was filtered to recover the catalyst. Finally, the acetone was removed from the collected filtrate using a rotary evaporator under reduced pressure at 50\(^\circ\)C, and the resulting viscous liquid product was designated de-polymerized organosolv lignin (DOL). The yield of DOL in this reductive de-polymerization process was 85 (±2) %.
4.3.3 Experimental Design

The process optimization for maximizing the yield and epoxy content of the lignin-based epoxy resin was carried out by central composite design (CCD) with 3 variables. Unlike a full factorial design, just 20 experimental runs were performed according to the CCD. This design contains 8 cube points, 6 axial points and 1 center point (Figure 4-1). For the center point, 6 replicate runs were conducted to check the reproducibility. The three independent variables considered were the NaOH/DOL molar ratio, reaction temperature and reaction time. The range of these three parameters were chosen based on our preliminary experiments and on the literature [27]. The variables and their levels selected for this study are shown in Table 4-1.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Unit</th>
<th>Term</th>
<th>Coded level of variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH/DOL molar ratio</td>
<td>-</td>
<td>Xi</td>
<td>-1.682, -1, 0, 1, 3, 5, 6.364</td>
</tr>
<tr>
<td>Reaction temperature</td>
<td>°C</td>
<td>X2</td>
<td>36, 50, 70, 90, 104</td>
</tr>
<tr>
<td>Reaction time</td>
<td>h</td>
<td>X3</td>
<td>1.7, 3, 5, 7, 8.3</td>
</tr>
</tbody>
</table>

Figure 4-1 Central composite design for K=3.
4.3.4 Epoxidation of the De-Polymerized Lignin

The synthesis of bio-based epoxy resins were conducted in a three-neck glass reactor (250 ml) based on the conditions that were designed by CCD. Totally 20 tests were performed and 20 samples were obtained by changing three independent parameters including sodium hydroxyl/DOL molar ratio from 0.364 mol/mol to 6.364 mol/mol, reaction temperature from 36°C to 104°C and reaction time from 102 min to 8h and 18 min. In a typical run, the DOL and epichlorohydrin (ECH, 6 ECH/DOL molar ratio, the average molecular weight of monomers of lignin is 180g/mol), distilled water and tetrabutylammonium bromide (TBAB, 2 wt.% of DOL) as a phase transfer catalyst were charged into the reactor. The reactor was heated in an oil bath under stirring to 80°C for 1 h reaction. Then, an adequate amount of NaOH solution was added dropwise to the reactor in 15 min and when the temperature reached the required temperature and allowed to react over a pre-specified length of time. Afterwards, the organic phase was separated and weighed to determine the mass balance of reaction. Then, the non-reacted excess ECH was separated from the organic phase by rotary evaporation at 100 °C under reduced pressure. The obtained epoxy resins were dissolved in acetone, and the salts (NaCl and TBAB) were filtered and bio-based epoxy resins were obtained by removal of acetone by rotary evaporation at 50 °C under reduced pressure and then dried in a vacuum oven at 60°C overnight to remove all volatile components. The synthesized epoxy resins were weighed to determine the yield of the epoxidation product.

4.3.5 Analytical Methods

Proton nuclear magnetic resonance (H-NMR) spectra were acquired at 25°C on a Varian Inova 600 NMR spectrometer equipped with a Varian 5 mm triple-resonance indirect-detection HCX probe. A total of 16–32 scans were accumulated using a 2 s recycle delay, 3.6 s acquisition time, a 45-degree tip angle (pw = 4.8 us), and a spectral width from 2 ppm to 14 ppm (sw = 9000.9 Hz). H-NMR analysis was performed on acetylated OL and acetylated DOL to determine the number of phenolic groups. Acetylation reaction was performed using acetic anhydride in the presence of pyridine as a basic catalyst. In a typical acetylation process, 1 g of dried OL or DOL was dissolved in 10 mL of mixture of acetic anhydride and pyridine (1:1 (v/v)) in a closed vial and mixed in a shaker at 40°C for 48 h. Then, the mixture was transferred into a beaker containing 100 ml of HCl solution (1 wt%) and the acetylated sample was precipitated in the acidic solution. The precipitated sample was separated and washed with distilled water several times to reach a pH 7. Finally, the
sample was dried in a vacuum oven at 80°C for 24 h to remove the residual water before further analysis. For quantitative H-NMR, 15 mg of acetylated sample was dissolved in Chloroform-d and 10 mg of dibromomethane (CH₂Br₂) as an internal standard.

The synthesized bio-based epoxy resins were analyzed by Nicolet 6700 Fourier Transform Infrared Spectroscopy (FT-IR) with Smart iTR™ ATR accessory in the range of 500-4000 cm⁻¹ to confirm the presence of epoxy groups in the structure of lignin. The average molecular weight and polydispersity index (PDI) of original organosolv lignin and the de-polymerized organosolv lignin (DOL) were determined using a Waters Breeze GPC-HPLC instrument (1525 binary pump, UV detector set at 270 nm, Waters Styragel HR1 column at 40°C) using THF as the eluent at a flow rate of 1 ml/min with linear polystyrene standards for the molecular weight calibration curve. The epoxy content (EC, weight percent epoxide) of the synthesized epoxy samples was measured by potentiometric titrator based on ASTM D1652-11. In this method, the resins dissolved in 30 mL of methylene chloride (MECL) and 15 mL of tetraethylammonium bromide (TEAB) solution in acetic acid the resulting solution is titrated with perchloric acid solution. As the reaction progresses, the potential of the solution gradually increases until the reaction approaches to completion at which point the potential increases very quickly. This equivalence point of titration was used to calculate the epoxy content (EC) of resin as follows:

\[ EC = \frac{4.3 \times V \times N}{W} \]  
(4-2)

Where V is the actual mL perchloric acid used to reach equivalence point, N is normality of perchloric acid reagent, W is the weight of the sample used and 4.3 is the theoretical molecular weight of the epoxide ring, 43, and it is adjusted to 4.3 for the calculation to percent epoxide.

The yield of the epoxidation product, i.e., the lignin-based epoxy resin, was calculated as follows:

\[ Yield \% = \frac{S}{L(1+0.301)} \times 100 \]  
(4-3)

where S is the weight of dried epoxidized lignin, L is the weight of dried DLO in each epoxidation run, and 0.301 g is the stoichiometric amount of epichlorohydrin for 1g of DOL.
4.4 Results and Discussion

4.4.1 Characteristic the Chemical Structure of OL and DOL

Organosolv lignin was chemically modified via the de-polymerization process as described previously before being used for the epoxidation reaction. H-NMR and GPC were used to investigate the effects of de-polymerization process on lignin structure and molecular weight. Figure 4-2 shows the H-NMR spectra of acetylated OL and acetylated DOL. The spectra of both samples have two peaks at 4.9 ppm and 7.26 ppm which are attributed to diboromethane (as an internal standard) and d-chloroform (as a solvent), respectively. The peaks associated with the protons of aliphatic acetates and phenolic acetates groups are at 1.6-2.2 ppm and 2.2-2.6 ppm, respectively [16]. The internal standard and solvent were selected in order to prevent any overlapping with the signals of aliphatic and aromatic acetates. In the H NMR spectra, the total integrated peak area of aliphatic and aromatic acetates was normalized with the integrated peak area of diboromethane to calculate the moles of total hydroxyl groups. The total hydroxyl groups of OL and DOL per lignin unit (180 g per unit) were found to be 0.764 and 0.974, respectively. From GPC measurement, the average molecular weight and polydispersity index (PDI) of OL were 2638 g/mol and 3.58, respectively. After the de-polymerization process, the M_w of lignin decreased to 760 g/mol with a narrower PDI of approximately 2. These results suggest that the de-polymerization process effectively cleaved the intermolecular bonds, such as ether bonds, which decreased the molecular weight of lignin, increased the content of total hydroxyl groups in DOL, and hence greatly promoted the reactivity of the DOL for epoxidation reaction.
Figure 4.2 H-NMR spectra and signal assignments of acetylated OL and acetylated DOL.

4.4.2 Characterization of the Chemical Structure of Epoxidized DOLs

The FTIR spectra of DOL and epoxidized DOLs are presented in Figure 4-3. All spectra were normalized based of C=C Aromatic bonds that are expected to be of no changes in all samples to provide better comparison of chemical changes caused by the epoxidation reaction. As the spectra of all epoxidized DOLs were similar, only some of them were shown here. All samples show a strong absorption band between 3200 and 3550 cm\(^{-1}\) which is associated with O-H stretch vibration of phenolic and aliphatic hydroxyl groups, with a prominent C-H stretching absorption at around 2900 cm\(^{-1}\) [26,28]. The absorption of other functional groups such as C=C aromatic bands and C=O groups are at 1600 cm\(^{-1}\) and 1740 cm\(^{-1}\), respectively. The presence of a peak at 915 cm\(^{-1}\) for the DOLs is attributed to epoxy groups, which is a proof of grafting epoxy groups to DOL through epoxidation reaction. The intensity of the peaks at 915 cm\(^{-1}\) indicates the content of epoxy groups on the synthesized samples. For instance, this peak in some samples such as A2, A6, A10 and A11
is sharper than other samples. These results are in good agreement with the measured epoxy content (EC) that is presented in Table 4-2.

![FTIR spectra of the DOL and the epoxidized DOLs.](image)

**Figure 4-3** FTIR spectra of the DOL and the epoxidized DOLs.

4.4.3 Model Building and Analysis of Variance (ANOVA)

The yield and the epoxy content of the lignin-based epoxy products from all synthesis runs based on the experimental design were measured and the results are presented in Table 4-2. These results show that the yield of epoxidation and epoxy content of the lignin-based epoxy products change with the variation of the synthesis conditions.
Table 4-2 Central composite matrix and output responses.

<table>
<thead>
<tr>
<th>Run #</th>
<th>Coded value</th>
<th>Actual value</th>
<th>Output responses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X₁</td>
<td>X₂</td>
<td>X₃</td>
</tr>
<tr>
<td>A1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>A2</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>A3</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>A4</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>A5</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>A6</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>A7</td>
<td>-1</td>
<td>1</td>
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</tr>
<tr>
<td>A8</td>
<td>1</td>
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<td>A10</td>
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<td>0</td>
</tr>
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<td>-1.682</td>
<td>0</td>
</tr>
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<td>1.682</td>
<td>0</td>
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<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>A14</td>
<td>0</td>
<td>0</td>
<td>1.682</td>
</tr>
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<td>A16</td>
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<td>0</td>
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</tr>
<tr>
<td>A19</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A20</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The Central Composite Design (CCD) was applied to optimize the synthesis condition of lignin-based epoxy resin and probe the relative or interactive effects of NaOH/DOL molar ratio, reaction temperature and reaction time on the yield of grafting reaction and epoxy content of the obtained epoxy samples. The responses were developed with various functions such as linear, quadratic and cubic models to find the best fitting model, and a quadratic equation based on the coded value of experimental factors was found to best fit the responses. The significance of the coefficients were evaluated based on a confidence interval of 95% where the corresponding \( P \)-value > \( \alpha = 0.05 \). The coefficients with \( P \)-value lower than 0.05 have a statistically significant effect on the responses, otherwise, the influence of others terms would be insignificant and removed from the regression model. The final reduced model to predict the yield and epoxy content of lignin-based epoxy resin are shown as follows:

\[
Yield \, (\%) = 90.63 + 5.05X_1 + 7.64X_2 + 4.22X_3 + 1.29X_1^2 \\
+ 1.67X_2^2 + 2.13X_3^2 + 2.54X_1X_2 - 1.21X_1X_3 + 1.75X_2X_3
\]

(4-4)

\[
EC = 3.20 + 1.46X_1 - 1.27X_2
\]

(4-5)

where \( X_1 \) is the coded value of NaOH/DOL molar ratio, \( X_2 \) is the coded value of reaction temperature and \( X_3 \) is the coded value of reaction time. The positive term indicates a synergistic effect on the responses while the negative coefficient indicates an antagonistic effect on the responses. The built model for the yield of epoxidation product is very complex and all terms including linear, square and interaction factors are significant. It was observed that all coefficients from the model gave positive effect except the interaction term of NaOH/DOL molar ratio and reaction time (\( X_1X_3 \)) that has a negative effect on the yield. As a result, a higher temperature, longer reaction time and larger NaOH/DOL molar ratio all lead to a higher yield of the epoxidation product. Obviously, harsh reaction conditions promote the grafting of epichlorohydrin into the structure of lignin. In contrast, the epoxy content has a linear relationship with the NaOH/DOL molar ratio (\( X_1 \)) and the reaction temperature (\( X_2 \)), while the effects of other factors are not significant on the epoxy content (EC) of the lignin-based epoxy resins. From equation (4-5), increasing NaOH/DOL molar ratio increases the epoxy content by 1.46 times and increasing the reaction temperature decreases the epoxy content by 1.27 times.
To evaluate the validity and suitability of the regression models, the analysis of variance (ANOVA) and the $F$-test were applied. The ANOVA results for the yield and epoxy content of the reaction products are presented in Tables 4-3 and 4-4, respectively. Statistical analysis for the yield shows that the $P$-value of the model is less than 0.05 which confirms the significance and the desirability of the model for the prediction. The “lack of fit” for the model is not significant as its $F$-value is 4.22 and its $P$-value is greater than the confidence interval ($P$-value > 0.05). The non-significant “lack of fit” is desirable because it can be used as a tool to confirm the good fit of the model. The coefficient of determination ($R^2$) for the epoxy product yield is very high, $R^2 = 0.9992$, indicating that 99.92% of variations of the yield can be explained by the independent variables. The value of adjusted $R^2$ is 0.9986 which is a bit lower than $R^2$ which again demonstrates the significance of model and indicates that the model is not over-fitted. Furthermore, the predicted $R^2$ is 0.9948, demonstrating a good agreement between the predicted values of the fitted model and the actual experimental values (Figure 4-4(a)).

As shown in Equation (4-5), the reduced model for EC is a linear model depending mainly on the NaOH/DOL molar ratio and the reaction temperature. If these most effective parameters remain unchanged, the effect of changing reaction time on EC is not significant. The ANOVA analysis on the quadratic model for EC is shown in Table 4-4. A $P$-value less than 0.05 indicates that the model is statistically significant to predict the EC value. Another way to evaluate the applicability of the predicted model is the $>0.05$ $P$-value of “Lack of fit”, meaning less significant. The regression model has a high coefficient of determination 0.9748. According to Table 4-4, the adjusted $R^2$ and predicted $R^2$ are 0.9658 and 0.9199, respectively, which confirm the adequacy of the model to elucidate the real effect of synthesis parameters on EC (Figure 4-4(b)).
Table 4-3 ANOVA results of the quadratic model for the yield of reaction.

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Mean squares</th>
<th>F value</th>
<th>P value (prob &gt; F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>9</td>
<td>1586.47</td>
<td>176.274</td>
<td>1475.15</td>
<td>0.000</td>
</tr>
<tr>
<td>Residual</td>
<td>10</td>
<td>1.19</td>
<td>0.119</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>5</td>
<td>0.97</td>
<td>0.193</td>
<td>4.22</td>
<td>0.070</td>
</tr>
<tr>
<td>Pure error</td>
<td>5</td>
<td>0.23</td>
<td>0.046</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>19</td>
<td>1587.66</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$R^2$ of the model is 0.9992; adjusted $R^2 = 0.9986$; predicted $R^2 = 0.9948$.

Table 4-4 ANOVA results of the quadratic model for the EC.

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Mean squares</th>
<th>F value</th>
<th>P value (prob &gt; F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
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<td>51.0804</td>
<td>10.2161</td>
<td>108.34</td>
<td>0.000</td>
</tr>
<tr>
<td>Residual</td>
<td>14</td>
<td>1.3202</td>
<td>0.0943</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>3</td>
<td>0.6068</td>
<td>0.1385</td>
<td>3.12</td>
<td>0.070</td>
</tr>
<tr>
<td>Pure error</td>
<td>11</td>
<td>0.7134</td>
<td>0.0649</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>19</td>
<td>52.4006</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$R^2$ of the model is 0.9748; adjusted $R^2 = 0.9658$; predicted $R^2 = 0.9199$. 
Figure 4-4 Comparison between the experimental and predicted values of epoxidation product yield (a) and EC (b).

The other evidences to prove the adequacy of models are the normal probability and residual plots, depicted in Figures 4-5 and 4-6 for yield and epoxy content, respectively. Figures 4-5(a) and 4-6(a) show the data points consistently appear on a straight trend line, i.e., the errors are normally distributed, indicating good prediction by the model. Figures 4-5(b) and 4-6(b) show the residual values versus the fitted values for each response. The randomly scattered residuals further prove the adequacy of the models.
Figure 4-5 Normal probability plot (a) and residuals vs. fitted values of the regression for product yield (b).
Figure 4-6 Normal probability plot (a) and residuals vs. fitted values of the regression for epoxy content of lignin-based epoxy resin (b).

4.4.4 Response Surface Plot and Optimization of Variables

The 3-dimensional plots and contour plots for the product yield and epoxy content are respectively shown in Figures 4-7 and 4-8. These plots show the effect of different parameters on the responses and they have a good agreement with the results obtained from the regression equations (4-4) and (4-5). These plots were used to optimize the values of different variables to maximize the yield and epoxy content of lignin-based epoxy resins simultaneously.

Figure 4-7A illustrates the interaction of reaction temperature and NaOH/DOL molar ratio on the yield at a constant reaction time. It is clearly shown that at a constant reaction temperature, with the increase of NaOH/DOL molar ratio, the yield of reaction generally increases. At lower temperatures, the yield remains constant while at a high reaction temperature, the yield increases drastically to as high as 150%. The combined effects of reaction time and NaOH/DOL molar ratio
on the yield are shown in Figure 4-7B. For a given reaction time, the yield increases by increasing NaOH/DOL molar ratio. Figure 4-7C shows the interactive impact of reaction time and reaction temperature on the yield at a constant NaOH/DOL molar ratio. At constant reaction time, the yield increases with increasing reaction temperature. As a common finding, all these three parameters (reaction time, temperature and NaOH/DOL molar ratio) have a positive effect on the product yield.
Figure 4-7  Response surface plots and contour plots of effects of different parameters on the product yield: effects of NaOH/DOL molar ratio and reaction temperature (A); effects of NaOH/DOL molar ratio and reaction time (B); effects of reaction time and temperature (C).

Figure 4-8A illustrates the interaction of reaction temperature and NaOH/DOL molar ratio on the epoxy content of the synthesized samples. At a constant NaOH/DOL molar ratio, increasing the
reaction temperature leads to a decrease in the epoxy content. The effects of reaction time and reaction temperature on the EC are shown in Figure 4-8B. When keeping the NaOH/DOL molar ratio constant, an increase of the reaction time does not significantly affect the EC response. This trend is in a good agreement with the regression model (Equation 4-5) indicating the interaction of reaction time and NaOH/DOL molar ratio is insignificant. Figure 4-8C shows the influences of reaction time and reaction temperature on the EC. Similar to those indicated in Figure 4-8B, the results shown in Figure 4-8C demonstrate that the interaction of reaction time and temperature are not significant on the EC response too.
Figure 4-8 Response surface plots and contour plots of effects of different parameters on the epoxy content of the epoxidation product: effects of NaOH/DOL molar ratio and reaction temperature (A); effects of NaOH/DOL molar ratio and reaction time (B); effects of reaction time and temperature (C).
Process optimization was performed with the response surface methodology to maximize the yield and epoxy content of the lignin-based epoxy products. The recommended optimal conditions were 8h, 55°C and a NaOH/DOL molar ratio of 6.3, where the predicted values of the product yield and epoxy content are 100% and 7.8, respectively. A new sample was synthesized at the above optimal conditions, and the resulting reaction yield and epoxy content were 99% and 8, respectively. Thus, the predicted values and experimental results are in a very good agreement. As such, the recommended optimal conditions obtained by response surface methodology can be verified and validated.

4.5 Conclusions

Epoxy resin was synthesized using de-polymerized organosolv lignin (DOL) in various conditions. The effects of the variable parameters including reaction time, reaction temperature and NaOH/DOL molar ratio on the reaction yield and epoxy content were investigated using central composite design. The obtained polynomial equations can be used to predict the yield and epoxy content of the products. The optimum conditions were predicted and validated by the experimental data. The optimum conditions determined are 8h at 55°C with 6.3 NaOH/DOL molar ratio, obtaining a lignin-based epoxy resin with a high epoxy content of ~8 and 99% reaction yield.
4.6 References


Sustainable Lignin-based Epoxy Resins Cured with Aromatic and Aliphatic Amine Curing Agents: Curing Kinetics and Thermal Properties
Abstract

Lignin-based epoxy resins were synthesized by reacting de-polymerized organosolv lignin (DOL) or de-polymerized kraft lignin (DKL) with epichlorohydrin under alkaline condition in the presence of a phase transfer catalyst. The synthesized lignin-based epoxy resins were cured with 4,4’-diaminodiphenyl methane (DDM, an aromatic amine) and diethyleneetriamine (DETA, an aliphatic amine) to generate a 3-dimensional cross-linked structure. The effects of curing agents on the curing process were investigated by non-isothermal differential scanning calorimetry (DSC). The dependency of activation energy of the curing reaction on the extent of curing (conversion) was determined in this study by model-free kinetics based on the DSC results. In addition, it was found that the thermal stability of the cured lignin-based epoxy resins were also influenced by the type of curing agents and the types of lignin used in synthesis of the bio-based epoxy resins.
5.1 Introduction

Epoxy resins are known as very versatile thermosetting resins which are used in a wide variety of applications such as adhesive, high performance composite, coatings and electronics [1–4] due to their unique characteristics including excellent chemical resistance, high moisture and solvent resistances, good thermal and dimensional stabilities, high adhesion strength, superior electrical properties, etc. [2,5]. Epoxy resins were first commercialized in 1946 [6] and around 45-50 percent of the worldwide production of epoxy resins are used in surface coating industries [7]. The production of epoxy resins has long relied upon fossil fuel resources to provide starting raw materials i.e. bisphenol A and epichlorohydrin. Around 67 percent of molar mass of conventional epoxy resins (i.e. diglycidyl ether of bisphenol A (DGEBA)) is bisphenol A (BPA) derived from fossil fuels [8]. However, increasing health and the environmental concerns over using BPA, due to its toxicity and carcinogenic effects, have been raised in recent decades [8]. On the other hand, the huge usage of fossil fuels is considered as a large contributor to the global warming and the climate change [9,10], and the fossil fuels are depleted, which in collection have encouraged scientists and researchers to find an alternative resources to produce polymeric materials [11]. Therefore, there is an arousing interest in seeking green alternative to BPA for developing bio-based and eco-friendly epoxy resins.

Various biomass resources such as plant oils [12], rosin[13], gallic acid [14], tannins [15,16], itaconic acid [8], lignin [17–19] have been used in synthesis of epoxy resins. Among these resources, lignin has demonstrated by many studies to be one of the most promising candidates for replacement of bisphenol A in production of bio-based epoxy resins, as it has aromatic structure with hydroxyl, carboxylic acid and phenolic functional groups that can react with epichlorohydrin to form bio-based epoxy resins [20,21]. Quite a few other studies have been reported on utilization of lignin in epoxy resin production [17,22,23]. However, only a small portion of the research focused on curing kinetics of lignin-based epoxy resins. It is well known that for any thermosetting polymer system, the final properties of the thermosetting resin would depend upon both the chemical structure and the curing process [24]. Thus, it is of significance to investigate on the curing process and kinetics for the lignin-based epoxy resin in order to provide products with excellent performance.
Sun et al.[24,25] studied the curing kinetics of lignin-based epoxy resins with three various curing agents including methylhexa-hydrophthalic anhydride, maleic anhydride and 2-methyl-4-methylimidazole using a DSC. The kinetics parameters were evaluated based on Kissinger method and autocatalytic model. Hirose et al. [26] determined the activation energy by Ozawa method for curing of bio-based epoxy resins synthesized with polyester chains derived from biomass components including saccharides, lignin and glycerol. In some studies, lignin was blended with epoxy resin and the curing kinetics of the mixture were studies. For example, Kong et al. [1] blended a conventional epoxy resin with a hydrolyzed lignin at 5% blending ratio, and investigated the curing kinetics and the bonding properties of the resins as adhesives. The results revealed that the introduction of a small amount of lignin promoted the curing process of the epoxy resin and improved the shear strength. Yin et al. [27] studied the mechanical properties and curing of an epoxy resin mixed with enzymatic hydrolysis corn straw lignin. The study of Yin et al. [27] suggested that the hydroxyl and carboxyl groups of lignin could react with the epoxy groups, and the polyphenol structure of lignin could catalyze the curing reaction.

The aim of this work was to investigate the curing behavior and kinetics of 100% lignin-based epoxy resins derived from de-polymerized organosolv lignin and de-polymerized kraft lignin, cured with two different curing agents. Differential Scanning Calorimetry (DSC) was used to monitor the curing behavior and the obtained data were evaluated by three model free methods i.e. Friedman, Vyazovkin, and Kissinger. In addition, thermal stability of the cured lignin-based epoxy resins was studied by thermogravimetric analysis (TGA).

5.2 Kinetic Analysis

In general, the rate of reaction can be expressed as a function of temperature, \( f(T) \), and degree of curing or conversion, \( f(\alpha) \), (Eq. 5-1) [28]. The functionality of temperature can be described by Arrhenius equation [29], while, the functionality of conversion depends on the mechanism of the curing reaction.

\[
\frac{d\alpha}{dt} = f(T) \times f(\alpha) = A \exp\left(-\frac{E}{RT}\right) f(\alpha)
\]  

(5-1)

where \( A \) is the pre-exponential factor, \( E \) is the activation energy, \( R \) is the universal gas constant and \( T \) is the temperature. The kinetic parameters can be calculated without any assumption of \( f(\alpha) \) by using model-free methods. The common method to evaluate the overall apparent activation
energy is the Kissinger method. Kissinger model can be presented by Eq. (5-2) [30].

\[
\ln \left( \frac{\beta}{T_{p,i}^2} \right) = \text{Const.} - \frac{E}{RT_{p,i}}
\]  

(5-2)

where \( \beta \) is the heating rate, \( T_p \) is the peak temperature, the subscript \( i \) denotes different heating rates. The overall activation energy can be obtained from the slope of plot of \( \ln(\beta/T_{p,i}^2) \) against \( 1/T_p \). A limitation of the Kissinger method is that it cannot predict the mechanism of the curing reaction throughout the curing process. However, the curing of an epoxy resin is known as a multi-step reaction [31,32] and a specific activation energy is associated with each step. Therefore, model-free isoconversional methods have been used to determine the variation in the activation energy. In the isoconversional principle, the rate of reaction only depends on temperature at the constant extent of the curing conversion. At each conversion, the activation energy can be determined and the mechanism of crosslinking reaction can be explored [32]. The isoconversional methods are classified into two categories, i.e. differential and integral methods [33]. The well-known differential method is the Friedman method expressed by Eq. (5-3) [33].

\[
\ln \left( \frac{d\alpha}{dt}_{\alpha,i} \right) = \ln[\beta_i \frac{d\alpha}{dT}] = \ln[A_{\alpha} f(\alpha)] - \frac{E_{\alpha}}{RT_{\alpha,i}}
\]  

(5-3)

Hence, the slope of a plot of \( \ln [\beta \frac{d\alpha}{dT}] \) versus \( 1/T \) at a constant degree of conversion (\( \alpha \)) for a set of heating rates (\( \beta \)) gives the activation energy at the specific value of \( \alpha \).

One of the accurate integral methods is the advanced isoconversional method proposed by Vyazovkin and described as follows [34];

\[
\phi(E_{\alpha}) = \sum_{i=1}^{n} \sum_{j=1}^{n} J[E_{\alpha}, T_i(t_{\alpha})] J[E_{\alpha}, T_j(t_{\alpha})] \]  

(5-4)

where

\[
J[E_{\alpha}, T_i(t_{\alpha})] = \int_{t_{\alpha} - \Delta t_{\alpha}}^{t_{\alpha}} \exp \left[ -\frac{E_{\alpha}}{RT_i(t)} \right] dt
\]  

(5-5)

where the subscript \( i \) and \( j \) denote different heating rates and \( n \) is the total number of heating rates.
5.3 Experimental Section

5.3.1 Materials

Kraft lignin (KL, softwood) and organosolv lignin (OL, hardwood) used in this study were kindly provided from Lignol and FPInnovations, respectively. KL is the yellowish powder and its weight-average molecular weight is \( M_w \approx 8300 \text{ g/mol} \) (with a polydispersity index PDI ≈ 8.2) based on our GPC-UV analysis. While, OL is a dark brown powder with its \( M_w \approx 2600 \text{ g/mol} \) (and PDI ≈ 3.6). Other chemicals used in this study, including 5wt.% ruthenium supported on carbon (Ru/C) as the lignin de-polymerization catalyst, acetone, sodium hydroxide, ethylene glycol, epichlorohydrin (ECH), tetrabutylammonium bromide (TBAB), and curing agents (4,4’-diaminodiphenyl methane (DDM) and diehylenetriamine (DETA), as depicted in Figure 5-1) were purchased from Sigma-Aldrich and used without any further purification.

![Chemical structure of the curing agents, DDM and DETA.](image)

5.3.2 De-polymerization of Lignin

Organosolv lignin (OL) and Kraft lignin (KL) were de-polymerized before grafting of the epoxy groups. The process of de-polymerization of OL was described in details in Chapter 3 and our previous paper [35]. Briefly, the de-polymerization process for organosolv lignin was carried out in a 500ml Parr stirred autoclave reactor. In this process, 50 g organosolv lignin, 2 gr Ru/C (as a catalyst), and 150 g of acetone were loaded into the reactor. The reactor was then pressurized with \( \text{H}_2 \) to 100 bar and then heated up under stirring to 350°C. After a one-hour reaction at 350°C, the reactor was immediately quenched with water to stop further reaction. The liquid product was transferred to a previously weighed flask. Acetone was removed in a vacuum rotary evaporator at 50°C. The yield of the de-polymerized lignin was 85 (±2) %. Kraft lignin (KL) was de-polymerized by a low-pressure process at 260°C for 1 h reaction in the 500 ml Parr stirred autoclave reactor in the presence of ethylene glycol (EG). The resulted product after acid precipitation (\( \text{pH} = 2 \)) was filtered to collect de-polymerized kraft lignin (DKL). The filter cake was dissolved in acetone to remove insoluble residual. Finally, a vacuum rotary evaporator was used to recover acetone at 50
℃. The yield of DKL from this process was 83 (±3) %. The obtained DOL and DKL were then subject for analysis on a GPC for molecular weights and distribution and use as BPA substitute in the synthesis of epoxy resins, as described below.

5.3.3 Synthesis of Lignin-Based Epoxy Resins

4 g DOL or DKL was dissolved in 12 g epichlorohydrin (the molar ratio of DOL or DKL to ECH was 6, the average molecular weight of monomers of lignin is 180g/mol) and added to a three-neck round flask, followed by 12 ml distilled water and tetrabutylamunium bromide (TBAB, 0.2 wt.% of DOL). The reactor (equipped with a reflux condenser and a magnetic stirrer) was heated to 80 °C and maintained at this temperature for 1 h under stirring. Then, the system was cooled to 55 °C and sodium hydroxyl solution (NaOH/lignin molar ratio was 6.3) was added dropwise into flask in 15 min and kept at this temperature for 8h. By cooling the system into room temperature, the organic phase was separated and excess of epichlorohydrin was evaporated using a rotary evaporator at 100 °C under reduced pressure. The resultant epoxy resin product was dissolved in acetone and the by-products were filtered out with a glass fiber filter. The filtrate containing the lignin-based epoxy resin was evaporated on a rotary evaporator. The yields of epoxidation for DOL and DKL were 99% and 97%, respectively.

5.3.4 Sample Preparation for Kinetic Study

Lignin-based epoxy resins were heated to 80 °C to lower the viscosity of the resins. Then, a stoichiometric amount of curing agent (based on the stoichiometric ratio of amine group in the curing agent to the epoxy group in the resin) was added to resin. The liquid curing agent (i.e. DETA) was added directly, while the solid curing agent (i.e. DDM) was preheated before adding into the resin. The mixture was held at 80 °C for 1 min or longer to assure that the curing agent was dispersed sufficiently. Afterward, the mixture was quenched in an ice bath to prevent any further reaction before DSC measurements. Samples specifications and their names are given in Table 5-1.
Table 5-1 Samples specifications and their names.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Epoxy resin (g)</th>
<th>Curing agent (g)</th>
<th>Curing agent</th>
<th>Epoxy resin type</th>
</tr>
</thead>
<tbody>
<tr>
<td>DKL-DETA</td>
<td>100</td>
<td>2.7</td>
<td>DETA</td>
<td>DKL-Epoxy</td>
</tr>
<tr>
<td>DOL-DETA</td>
<td>100</td>
<td>3.8</td>
<td>DETA</td>
<td>DOL-Epoxy</td>
</tr>
<tr>
<td>DKL-DDM</td>
<td>100</td>
<td>6.5</td>
<td>DDM</td>
<td>DKL-Epoxy</td>
</tr>
<tr>
<td>DOL-DDM</td>
<td>100</td>
<td>9.2</td>
<td>DDM</td>
<td>DOL-Epoxy</td>
</tr>
</tbody>
</table>

5.3.5 Sample Preparation for Thermal Stability Study

In order to investigate the thermal stability of lignin-based epoxy resins, stoichiometric amount of epoxy resin and curing agent was mixed uniformly and cured in a preheated oven based on our DSC results that determined the maximum temperature of exothermic peak ($T_p$) and the end temperature of curing ($T_{end}$). To ensure fully curing of the resins, stoichiometric mixture of an epoxy resin and a curing agent was cured at its $T_p$ for 4 h and post-cured at $T_{end}$ for 90 min.

5.3.6 Characterization

The chemical structure of the de-polymerized lignins (DKL and DOL) and the lignin-based epoxy resins was analyzed by FTIR. The average molecular weights and polydispersity index of the de-polymerized lignins and the epoxidized de-polymerized lignins were measured using a Waters Breeze GPC-HPLC instrument (1525 binary lamp, UV detector set at 270 nm, Waters Styragel HR1 column at 40°C) using THF as the eluent at a flow rate of 1 ml/min, calibrated with linear polystyrene standards for molecular weight distribution.

The epoxy content of the synthesized lignin-based epoxy resins was determined with a potentiometric titrator (Titroline 7000 Titrator) according to ASTM D1652-11 standard. Briefly, 0.3-0.6 g of sample was placed in a 100 mL beaker and dissolved in 30 ml of methylene chloride and 15 ml of tetraethylammonium bromide solution in glacial acetic acid. The resulted solution was titrated with perchloric acid (0.1 N in glacial acetic acid). The normality of perchloric acid was determined before each measurement by 0.25 g of potassium acid phthalate.
Differential Scanning Calorimetry (DSC) was used to evaluate the curing behavior of lignin-based epoxy–amine systems. The DSC measurements were conducted on a Mettler Toledo DSC 1 under nitrogen flow rate of 50 ml/min. The mixture of an epoxy resin and a curing agent (6-7 mg) was placed in an aluminum DSC pan and sealed with an aluminum lid. The DSC measurements were performed from 25°C to 300°C at various heating rates: 4, 6, 8 and 10 °C/min. The thermal stability of the fully cured lignin-based epoxy resins was studied by thermal gravimetric analysis (TGA, Perkin Elmer Pyris 1). The measurements were carried out on 7-10 mg samples at 10 °C/min heating rate from room temperature to 800 °C under a nitrogen flow (50 mL/min).

5.4 Results and Discussion

5.4.1 Chemical Characteristics of the Lignin-Based Epoxy Resins

The chemical structure and the average molecular weights of the lignin-based epoxy resins and the corresponding de-polymerized lignins (DOL and DKL) as references were analyzed by FTIR and GPC, respectively. The normalized FTIR spectra are shown in Figure 5-2. The FTIR results were normalized based on C=C aromatic bonds at 1600 cm\(^{-1}\) which are expected to remain constant in all samples in order to provide better comparison of chemical structure between different samples. As widely agreed upon, the vibration of the epoxy groups in the synthesized resins is around 915 cm\(^{-1}\), and the broad band at 3200-3550 cm\(^{-1}\) corresponds to the vibration of hydroxyl groups. As observed, the intensity of peak in 3200-3550 cm\(^{-1}\) range decreases after the epoxidation process. In other words, the hydroxyl groups were consumed during the epoxidation reaction to form epoxy group as evidenced by the IR adsorption peak at 915 cm\(^{-1}\) band in the samples of DOL-epoxy resin and DKL-epoxy resin. Moreover, the intensity of hydroxyl groups is lower in DOL and DOL-epoxy resin in comparison with DKL and DKL-epoxy resin.
The GPC measurement results are summarized in Table 5-2. The average molecular weight (\(M_w\)) of the DKL is 1400 g/mol and its polydispersity index (PDI) is 2.4, and after the epoxidation reaction, the average molecular weight of DKL was doubled (2800 g/mol) with an appreciable increase in PDI (3.5). Similarly, the average molecular weight and PDI of the DOL increased from 760 to 1400 g/mol and from 2 to 2.8, respectively, after the epoxidation reaction. These results suggest that several lignin molecules attached to each other during the epoxidation reaction, leading to dramatic increase in the average molecular weights of epoxidized samples. In addition, the epoxy content of the synthesized epoxy resins are 5.6 and 8.0 for DKL-Epoxy and DOL-Epoxy, respectively, as measured by potentiometric titrator. A higher epoxy content for DOL-Epoxy than that of DKL-Epoxy suggests that DOL has better reactivity for the epoxidation reaction than DKL due to its lower molecular weight (Table 5-2).
Table 5-2 Average molecular weights, polydispersity index and epoxy content of the lignin-based epoxy resins.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(M_n)</th>
<th>(M_w)</th>
<th>PDI</th>
<th>Epoxy content</th>
</tr>
</thead>
<tbody>
<tr>
<td>DKL</td>
<td>580</td>
<td>1400</td>
<td>2.4</td>
<td>–</td>
</tr>
<tr>
<td>DKL-Epoxy</td>
<td>790</td>
<td>2800</td>
<td>3.5</td>
<td>5.6</td>
</tr>
<tr>
<td>DOL</td>
<td>370</td>
<td>760</td>
<td>2.0</td>
<td>–</td>
</tr>
<tr>
<td>DOL-Epoxy</td>
<td>500</td>
<td>1400</td>
<td>2.8</td>
<td>8.0</td>
</tr>
</tbody>
</table>

5.4.2 Differential Scanning Calorimetry Analysis

The non-isothermal DSC peak for curing of the lignin-based epoxy resins mixed with amine curing agents at different heating rates are shown in Figure 5-3. Tables 5-3 and 5-4 show a summary of the curing characteristics of lignin-based epoxy/DETA and lignin-based epoxy/DDM samples, respectively. In this study, non-isothermal experiments were carried out to prevent the vitrification phenomena during the curing of epoxy resins. The total curing heat was calculated by the integration of the exothermic curing peak. As a sample was cured completely at various heating rates, the total curing heat remains approximately constant at each heating rate with negligible difference. With increasing the heating rate, the onset temperature of curing \(T_{\text{onset}}\), the maximum temperature of exothermic peak \(T_p\) and the end temperature of curing \(T_{\text{end}}\) shifted to a higher temperature for a specific sample, which has been commonly observed in curing of a thermosetting resin, due to this fact that at a higher heating rate the resin sample has less time at a specific temperature which diminish the degree of curing at each temperature [36]. It can also be seen, the onset temperature of all systems are approximately at 30-50 ºC, which means that these systems could cure almost at room temperature. The total heat of curing of the DKL-based epoxy systems was lower than those of the DOL-based epoxy systems, which can be accounted for by the greater epoxy content of the DOL-epoxy than that of the DKL-epoxy, as shown in Table 5-2. Another possible explanation for this finding could be that the DKL-based epoxy resin is a solid material with a melting point of 60-70ºC. When endothermic melting and the curing reaction (exothermic) occurred simultaneously, the total heat of reaction could be reduced too.
Figure 5-3 DSC curves of the lignin based-epoxy resins cured with DETA and DDM at different heating rates.

Table 5-3 Curing characteristics of the lignin-based epoxy/DETA systems.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Heating rate (°C/min)</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_{\text{end}}$ (°C)</th>
<th>$T_{\text{peak}}$ (°C)</th>
<th>$\Delta H_{\text{total}}$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DKL-DETA</td>
<td>4</td>
<td>30.8</td>
<td>168.3</td>
<td>90.1</td>
<td>46.3</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>31.5</td>
<td>174.1</td>
<td>91.4</td>
<td>44.2</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>32.8</td>
<td>181.4</td>
<td>97.4</td>
<td>42.6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>33.3</td>
<td>188.0</td>
<td>102.1</td>
<td>43.1</td>
</tr>
<tr>
<td>DOL-DETA</td>
<td>4</td>
<td>28.2</td>
<td>168.5</td>
<td>87.4</td>
<td>137.8</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>30.0</td>
<td>172.9</td>
<td>92.2</td>
<td>138.5</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>31.0</td>
<td>180.2</td>
<td>94.1</td>
<td>148.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>32.3</td>
<td>200.2</td>
<td>101.0</td>
<td>140.1</td>
</tr>
</tbody>
</table>
Table 5-4 Curing characteristics of lignin-based epoxy/DDM systems.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Heating rate (°C/min)</th>
<th>(T_{\text{onset}}) (°C)</th>
<th>(T_{\text{end}}) (°C)</th>
<th>(T_{\text{peak}}) (°C)</th>
<th>(\Delta H_{\text{total}}) (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DKL-DDM</td>
<td>4</td>
<td>29.9</td>
<td>207.2</td>
<td>104.5</td>
<td>86.4</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>33.3</td>
<td>216.3</td>
<td>117.4</td>
<td>82.2</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>35.0</td>
<td>222.2</td>
<td>123.3</td>
<td>81.6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>38.8</td>
<td>229.2</td>
<td>127.5</td>
<td>84.3</td>
</tr>
<tr>
<td>DOL-DDM</td>
<td>4</td>
<td>45.0</td>
<td>222.1</td>
<td>128.0</td>
<td>182.8</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>49.5</td>
<td>228.7</td>
<td>136.5</td>
<td>177.9</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>51.8</td>
<td>233.4</td>
<td>143.1</td>
<td>176.8</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>54.4</td>
<td>239.9</td>
<td>145.0</td>
<td>180.1</td>
</tr>
</tbody>
</table>

5.4.3 Curing Kinetics

The DSC results were evaluated by different model-free methods. The overall activation energy of the lignin-based epoxy curing was determined by Kissinger method, as described previously in Eq. (5-2). Table 5-5 presents the overall activation energy for curing of various resin systems calculated based on Kissinger method. The overall activation energy of all resin systems is 40-82 kJ/mol, the typical range of the conventional epoxy resins [25,37–39]. As displayed in Table 5-5, the overall activation energies of both DOL and DKL-based epoxy resins cured with DETA are higher than those cured with DDM, suggesting that an aromatic amine has better activity than an aliphatic amine for curing of the lignin-based epoxy resins.

Table 5-5 Overall activation energy for curing of various resin systems based on Kissinger method.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Overall activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DKL-DETA</td>
<td>69.34</td>
</tr>
<tr>
<td>DOL-DETA</td>
<td>81.58</td>
</tr>
<tr>
<td>DKL-DDM</td>
<td>42.48</td>
</tr>
<tr>
<td>DOL-DDM</td>
<td>52.41</td>
</tr>
</tbody>
</table>
The reaction between epoxy and amine has been known as a multistep process and various reactions can occur during the curing process [40]. The curing process involves both the non-catalytic and autocatalytic reactions of primary and secondary amine with epoxide groups, as well as the etherification and homopolymerization reactions [28,38]. For a typical epoxy resin, its effective activation energy may vary in three stages. At the beginning of curing, the predominant reaction is between the primary amine and the epoxy group, at a relatively higher activation energy, while with increasing the extent of curing, the activation energy decreases to around 40-50 kJ/mol. This decrease in activation energy was believed to be associated with the change in the reaction mechanism from non-catalyzed to autocatalytic one [38,41,42]. Different trends of activation energy were reported in the last stage of epoxy-amine curing process (α > 0.7). Some studies [38,41,42] showed that the activation energy increases towards the end of reaction. However, a diverse trend was reported by Sbirrazzuoli et al. [37], Cai et al. [42] and Perrin et al. [28].

Since Kissinger method is not able to predict the above mentioned trends of activation energy with the extent of the curing process, and elaborate the mechanism of epoxy-amine curing reaction, Friedman method and the advanced isoconversional method proposed by Vyazovkin, as described by Eqs. (5-3) and (5-4) were used to evaluate variation of activation energy for all lignin-based epoxy-amine systems with extent of the curing process (conversion). The values of activation energy as a function of conversion are depicted in Figure 5-4. It can be seen that the overall trends of activation energy derived from both Vyazovkin and Friedman methods are in a good agreement with each other for all systems.

From the figure, it can be clearly observed that there are two distinct trends for the dependency of activation energy on the degree of curing extent (conversion) for the lignin-based epoxy resins cured with aliphatic and aromatic amines. In DKL-DETA and DOL-DETA systems, the activation energy remains approximately constant or decreases slightly when the degree of conversion is below 0.7. Afterwards, the activation energy drops dramatically. On the other hand, the activation energy of lignin-based epoxy resins cured with the aromatic amine (DDM) climbs slightly in the initial stage of curing (α < 0.75- 0.8 ) and rises drastically in the later stages. Almost in the whole conversion range, the activation energy of DKL-based epoxy resins is lower than DOL-based ones, which might be attributed to the chemical structure of DKL containing more hydroxyl groups. More hydroxyl groups could promote the curing process [28,38]. The increase of activation energy
with extent of curing for the lignin-based epoxy resins cured with DDM may be attributed to the following fact. DDM is a solid curing agent cannot be mixed homogeneously with the resin, which could make the curing process be controlled by the self-curing reactions, i.e., etherification or homopolymerization reactions, rather than by the autocatalytic reactions between amine and epoxide groups. These self-curing reactions have high activation energies (in a range of 97-170 kJ/mol [38]) and could be retarded while increasing the extent of curing (conversion) because partially cured resin molecules become more rigid, thus limiting the self-curing reactions and raising the curing activation energy. In contrast, the activation energy of DKL-epoxy or DOL-epoxy cured with the DETA generally decreases with increasing the curing conversion, and the activation energy at the late stage of the curing dropped to less than 30 kJ/mol, suggesting that the curing of these resins and DETA may be controlled by the autocatalytic mechanism.
Figure 5-4 Activation energy of the curing reaction versus conversion based on Friedman and Vyazovkin methods.

5.4.4 Thermal Stability

The thermal stability of the cured lignin-based epoxy samples was examined by TGA under N$_2$ condition. The TGA results and their first derivatives (DTG) are displayed in Figure 5-5. The initial decomposition temperature (IDT), the maximum rate decomposition temperature ($T_{\text{max}}$), the final decomposition temperature (FDT), yield of char at 800 ºC (Char$_{800}$), and the statistic heat-resistant temperature index ($T_s$) of all systems were obtained and summarized in Table 5-6. The statistic heat-resistant temperature index was calculated by Eq. (5-6).

$$T_s = 0.49(T_{d5} + 0.6(T_{d30} - T_{d5}))$$  \hspace{1cm} (5-6)
where, $T_{d5}$ and $T_{d30}$ are the temperature at 5% weight loss and 30% weight loss, respectively [11,43].

The TGA results indicate that (1) both DOL-based epoxy resins had faster weight loss in comparison with DKL-based epoxy resins, or in another word, the DKL-based epoxy resins are more thermally stable than the DOL-based epoxy resins; (2) The lignin-based epoxy samples cured with DDM curing agent have higher thermal stability than those cured with DETA. This behavior could be attributed to the aromatic structure of DDM that can stabilize the cured resins. In addition, the $T_s$ value of DKL-DDM is 179 °C, the highest among all samples. The thermal stability of all lignin-based samples is comparable to the thermal properties of the petroleum-based epoxy resins [11]. From Table 5-6, another interesting observation is that the char yields at 800 °C for all the lignin-based epoxy resins are in the range of 23-38%, much higher than of conventional BPA-based epoxy resins (e.g., DGEBA has 10% char yield at 800°C [11], 12.2% at 700°C [44] and 4.61% at 800°C [45]). The char yield of DKL-DDM at 800 °C is as high as 38%, suggesting that the DKL-DDM could be a promising substitute for the petroleum-based epoxy resins.

![TGA and DTG curves](image)

**Figure 5-5** Thermal stability of the cured lignin-based epoxy resins.
### Table 5-6 Thermal characteristics of the cured lignin-based epoxy resins.

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>IDT (ºC)</th>
<th>$T_{\text{max}}$ (ºC)</th>
<th>FDT (ºC)</th>
<th>$T_s$ (ºC)</th>
<th>Char$_{800}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cured DKL-DETA</td>
<td>252</td>
<td>406</td>
<td>482</td>
<td>165</td>
<td>33</td>
</tr>
<tr>
<td>Cured DOL-DETA</td>
<td>228</td>
<td>376</td>
<td>461</td>
<td>148</td>
<td>23</td>
</tr>
<tr>
<td>Cured DKL-DDM</td>
<td>290</td>
<td>416</td>
<td>508</td>
<td>179</td>
<td>38</td>
</tr>
<tr>
<td>Cured DOL-DDM</td>
<td>257</td>
<td>400</td>
<td>462</td>
<td>166</td>
<td>29</td>
</tr>
</tbody>
</table>

#### 5.5 Conclusions

This study evaluated the kinetics of curing bio-based epoxy resins derived from de-polymerized kraft lignin and de-polymerized organosolv lignin with an aromatic amine and an aliphatic amine, and thermal stability of the cured lignin-based epoxy samples. Some major conclusions are summarized below:

1. The overall activation energy of all resin systems is 40-82 kJ/mol. The overall activation energies of both DOL and DKL-based epoxy resins cured with DETA are higher than those cured with DDM, suggesting that an aromatic amine has better activity than an aliphatic amine for curing of the lignin-based epoxy resins.

2. Almost in the whole curing conversion range, the activation energy of DKL-based epoxy resins is lower than DOL-based ones, likely attributed to the chemical structure of DKL containing more hydroxyl groups, which promote the curing process.

3. For the lignin-based epoxy resins cured with DDM, the activation energy increases with increasing the curing extent, while the activation energy of DKL-epoxy or DOL-epoxy cured with DETA generally decreases with increasing the curing conversion. This difference might be attributed to different curing mechanisms.

4. The DKL-based epoxy resins are more thermally stable than the DOL-based epoxy resins. The lignin-based epoxy samples cured with DDM curing agent have higher thermal stability than those cured with DETA. However, the thermal stability of all lignin-based samples is comparable to the thermal properties of petroleum-based epoxy resins.

5. The char yields at 800 ºC for all the lignin-based epoxy resins are in the range of 23-38 %, much higher than of conventional BPA-based epoxy resins. The char yield of DKL-DDM
at 800 °C is as high as 38%, suggesting that the DKL-DDM could be a promising substitute for the petroleum-based epoxy resins.
5.6 References:


Curing Kinetics and Mechanical Properties of Bio-based Epoxy Resin Composites Comprising Lignin-Based Epoxy Resins
Abstract

Lignin-based epoxy resins derived from de-polymerized kraft/organosolv lignins were blended with a conventional bisphenol A (BPA)-based epoxy resin at various percentages to prepare bio-based epoxy composites as polymer matrices for manufacturing of fiber-reinforced plastics (FRPs). The curing process of epoxy composites was studied using differential scanning calorimetry (DSC) and the activation energy was calculated by Kissinger method and Friedman method. Epoxy composites comprising a low percentage (25 wt%) of lignin-based epoxy can be cured faster than the pure BPA-based epoxy used in particular at the early stage of curing. However, blending a large amount (>50 wt%) of lignin-based epoxy with the BPA-based epoxy retarded the curing process particularly at the late stage of curing. Tensile and flexural strengths of the prepared FRPs using bio-based epoxy composites were found to be superior or comparable to those of the FRP with the pure BPA-based epoxy when the lignin-based epoxy blending ratio is less than 50-75 wt%. Event for FRPs with bio-epoxy composites containing as high as 75-100 wt% of lignin-based epoxy, the mechanical properties (in terms of modulus of elasticity or flexural modulus) are comparable to the FRP with the pure BPA-based epoxy resin.
6.1 Introduction

In recent decades, synthesis of bio-based chemicals and materials using bio-renewable resources has drawn increasing attention in academia and industry due to the concerns over the environment impacts and the depleting reserves of fossil fuels (currently the dominant sources for chemicals and materials) [1–4].

Epoxy resin is one of the most widely used thermosetting polymers because of its superior properties, e.g., great chemical resistance, good thermal stability and high adhesion strength to various substrates. These properties provide diverse applications of epoxy resins in coatings, adhesives to other engineering applications [4–6]. The ultimate properties of epoxy resins are determined mainly by their chemical composition and their curing conditions [7,8]. Therefore, it is of great significance to investigate on the curing process of epoxy resins for better control of their final properties.

Synthesis of bio-based epoxy resins were reported in several literature studies. However, limited attention has been paid on simultaneous characterization of the curing kinetics of the resins and mechanical properties of fiber reinforced plastics (FRPs) using lignin-based epoxy matrices. Bio-resources including vegetable oil [9,10], tannins [11–13], rosin [14–16], bark [17], liquefied biomass [2,18] and lignin [19,20] have been used for the synthesis of bio-based epoxy resins. Kim et al. [21] reported a novel process for epoxidation of several plants oils without using solvent, and demonstrating that the epoxidized linseed oil have excellent modulus and impact resistance. Benyahya et al. [12] used the bio-phenols extracted from green tea leaves for the production of a bio-based epoxy resin. The cured resin sample exhibited high cross-link density and outstanding thermal and mechanical properties. Liu et al. [14] developed a 100% rosin-based epoxy resin possessing a high glass transition temperature of around 164ºC. Kuo et al [17] synthesized a bark-based epoxy resin exhibiting higher tensile strength and stiffness in comparison with other bio-based epoxy resins. Lignin was also demonstrated to be a promising bio-substitute for bisphenol A (BPA) in synthesis of bio-based epoxy resins with mechanical and thermal properties comparable to the conventional BPA-based epoxy resins [18,22].
As discussed in the previous chapters and described in our previous published work [23,24], a novel method has been developed for the synthesis of bio-based epoxy resins with reduced side reactions, employing de-polymerized lignin from kraft lignin (DKL) and de-polymerized organosolv lignin (DOL) under alkaline condition in the presence of a phase transfer catalyst, tetrabutylammonium bromide (TBAB). Lignin-based epoxy resins derived from de-polymerized kraft/organosolv lignins were blended with a conventional bisphenol A (BPA)-based epoxy resin at various percentages (25–100 wt%) to prepare bio-based epoxy composites. The curing mechanism and kinetics for the epoxy composites were studied based on differential scanning calorimetry (DSC) measurements. In addition, the epoxy composites were applied as polymer matrices for manufacturing of fiber-reinforced plastics (FRPs). The mechanical properties of these FRPs were examined with a universal testing machine (UTM) and by dynamic mechanical analysis (DMA).

6.2 Experimental

6.2.1 Materials

As detailed in previously chapters and our previous published work [23,24], two kinds of lignin-based epoxy resins were synthesized from de-polymerized kraft lignin (DKL, softwood) and de-polymerized organosolv lignin (DOL, hardwood), denoted as DKL-epoxy resin and DOL-epoxy resin, respectively. The synthesized DKL-epoxy resin is in black powder form with the average molecular weight (Mₘ) of 2800 g/mol and its epoxy content (EC, weight percent epoxide) is around 5.6. The prepared DOL-epoxy resin is a viscous liquid whose Mₘ and EC are 1400 g/mol and 8.0, respectively. Araldite® GZ 540 X 90, supplied from Huntsman, as a conventional bisphenol A (BPA)-based epoxy resin (DGEBA) was used in this study to prepare epoxy composites comprising the BPA-based epoxy resin and 25-100 wt% of the above lignin-based epoxy resin. The epoxy equivalent weight (EEW) and the solid content of this liquid BPA-based epoxy resin are approx. 295 g/eq and 90 wt% (containing 10 wt% of xylene solvent), respectively. Prior to the kinetic study, the BPA-based epoxy resin was completely dried in a vacuum oven to remove the xylene solvent. 4, 4’-Diaminodiphenylmethane (DDM) obtained from Sigma Aldrich was used as a curing agent for the epoxy resins. BGF fiberglass cloth (E-Glass, Plain weave fiber glass with 0.015 inches thickness) was purchased from Freeman, Ohio.
6.2.2 Sample Preparation for Kinetic Study

To prepare epoxy composites samples for kinetic study, the desire amount of lignin-based epoxy resin and the conventional BPA-based epoxy resin (DGEBA) were added into a vial and heated in an oil bath at 80 ºC. When the resin mixture was melted and its viscosity decreased, a stoichiometric amount of curing agent, i.e. diaminodiphenyl methane (DDM) in this work, was added into the vial and mixed for approximately 1 min at 80 ºC to ensure that the curing agent was dispersed sufficiently. Finally, the sample was immediately quenched in an ice bath to avoid any further reactions before DSC measurements. The sample names and specifications are shown in Table 6-1.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>DGEBA (g)</th>
<th>DOL-epoxy resin (g)</th>
<th>DKL-epoxy resin (g)</th>
<th>DDM (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA-DDM</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>16.8</td>
</tr>
<tr>
<td>25% DOL-DDM</td>
<td>75</td>
<td>25</td>
<td>0</td>
<td>14.9</td>
</tr>
<tr>
<td>50% DOL-DDM</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>75% DOL-DDM</td>
<td>25</td>
<td>75</td>
<td>0</td>
<td>11.1</td>
</tr>
<tr>
<td>100% DOL-DDM</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>9.2</td>
</tr>
<tr>
<td>25% DKL-DDM</td>
<td>75</td>
<td>0</td>
<td>25</td>
<td>14.2</td>
</tr>
<tr>
<td>50% DKL-DDM</td>
<td>50</td>
<td>0</td>
<td>50</td>
<td>11.7</td>
</tr>
<tr>
<td>75% DKL-DDM</td>
<td>25</td>
<td>0</td>
<td>75</td>
<td>9.1</td>
</tr>
<tr>
<td>100% DKL-DDM</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>6.5</td>
</tr>
</tbody>
</table>

1 Based on the stoichiometric ratio of amine group in the curing agent to the epoxy group in the resin.

6.2.3 Preparation of fiber-reinforced plastics (FRPs) using bio-based epoxy resins as polymer matrices

Fiber-reinforced plastics (FRPs) were prepared using epoxy composites as polymer matrices and fiberglass mat, according to ASTM D638-10 [25]. The desire amount of lignin-based epoxy resin, the conventional BPA-based epoxy resin and DDM as the curing agent were mixed based on specifications listed in Table 6-1. The fiberglass mat was cut into a rectangular shape with dimensions of 200 mm × 150 mm. The epoxy resin blend (containing varying percentage of lignin-based epoxy resin) was dissolved in a small amount of acetone and applied uniformly with a brush.
on the pre-cut fiberglass mat placed in a release bag. This step was repeated 10 times to reach an approximate thickness of 3 mm (containing 10 layers of the fiberglass mat). Then, the bio-based epoxy composites left for 3 hours before curing. Afterward, the bio-based epoxy composites were placed in a hot press and cured at respective curing conditions as determined in the previous chapter, in terms of the peak curing temperature ($T_p$) and the end-set curing temperature ($T_{end}$). Generally, each composite sample was pressed on a hot-press under 2000 psi at its $T_p$ for 1 h and then at its $T_{end}$ for 45 min. The obtained composites were all post-cured at $T_{end}$ for 5 hours in a pre-heated oven.

6.2.4 DSC Measurements

The DSC measurements were performed on a Mettler Toledo DSC 1 to investigate the curing behavior of the epoxy composites (containing various percentages of lignin-based epoxy resin). The DSC measurements were carried out under a constant flow of nitrogen of 50 ml/min. For each DSC run, small quantities of the epoxy resin blend and the curing agents (7-8 mg in total) were sealed in an aluminum DSC pan. The DSC measurements were conducted at various heating rates of 4, 6, 8, 10°C/min over a temperature range of 25°C to 330°C. The samples cured at 10°C/min were cooled to the room temperature and then re-heated to 350°C at 10°C/min to measure the glass transition temperature ($T_g$) of the cured epoxy composites.

In the DSC measurements, it is assumed that the extent of consumption of the reactive groups is proportional to the amount of heat evolved. The degree of conversion or extent of the curing reaction ($\alpha$) and the reaction rate as a function of time can be calculated from the DSC data by the following equations [26,27]:

$$\alpha = \frac{H_t}{H_T}$$  \hspace{1cm} (6-1)

$$\frac{d\alpha}{dt} = \left(\frac{1}{H_T}\right) \frac{dH}{dt}$$  \hspace{1cm} (6-2)

where $\alpha$ denotes the degree of conversion, $H_t$ is the enthalpy of the reaction within time $t$, $H_T$ is the total enthalpy of the reaction for a fully cured sample, $d\alpha/dt$ is the rate of reaction and $dH/dt$
is the heat flow rate. The enthalpy of reaction up to time \( t \) can be calculated by integration of the heat flow over the time \( t \) of the exothermic peak from DSC.

In this study, two model-free methods were used to analyze the dynamic DSC data. The first method is Kissinger method, which determines the overall activation energy. The following equation can be expressed based on the Kissinger method [28,29]:

\[
\ln\left(\frac{\beta}{T_{p,i}^2}\right) = \text{Const.} - \frac{E}{RT_{p,i}}
\]

(6-3)

where \( \beta \) is the heating rate, \( T_p \) is the peak curing temperature, the subscript \( i \) is ordinal number of DSC runs performed at different heating rates. The overall activation energy can be obtained from the slope while plotting \( \ln(\beta/T_{p,i}^2) \) vs. \( 1/T_p \). The second method is a differential isoconversional method originally presented by Friedman, which enable calculation of activation energy of the curing reaction at any particular extent of conversion (\( \alpha \)) by the following equation [30,31]:

\[
\ln\left[\frac{d\alpha}{dT}\right]_{\alpha,i} = \ln[\beta_i \frac{d\alpha}{dT}] = \ln[A_{\alpha} f(\alpha)] - \frac{E_{\alpha}}{RT_{\alpha,i}}
\]

(6-4)

Hence, the slope of the plot of \( \ln [\beta \, d\alpha/dT] \) vs. \( 1/T \) at constant degree of conversion (\( \alpha \)) for a set of heating rates (\( \beta \)) gives the activation energy at the specific value of \( \alpha \).

### 6.2.5 Mechanical Properties Tests

Tensile tests of the prepared FRPs using bio-based epoxy resins were performed on a Universal Testing Machine Model Instron 8800 with a load cell of 250kN at a crosshead speed of 5 mm/min and the gage length of 50 mm in accordance to ASTM D638-10 [25]. A 50mm extensometer was used to accurately measure the strain to obtain modulus. The FRP panels were cut into dumbbell-shaped specimens, based on ASTM D638-10, as shown in Figure 6-1.
For the flexural tests, the FRP specimens were cut into rectangular samples of dimensions of 3.2 mm × 12.7 mm × 127 mm in accordance to ASTM D790-10 [32]. The measurements were conducted on another set of Universal Testing Machine (Admet 7000) in three-point bending mode at 25ºC with a strain rate of 1.5 mm/min and span length of 48 mm. Five measurements were conducted for each sample and the mean value was reported. In 3-point bending experiments, the flexural modulus (E, GPa) and flexural strength (σ, MPa) are defined by Eqs. (6-5) and (6-6), respectively:

\[
E = \frac{L^3 F}{4wh^3 d} \quad (6-5)
\]

\[
\sigma = \frac{3FL}{2wh^2} \quad (6-6)
\]

where \(L\) is the length of the support span (mm), \(F\) is the load (force) at the fracture point (N), \(w\) and \(h\) are the width (mm) and thickness (mm) of beam, respectively, and \(d\) is the deflection due to the force applied at the middle of the beam.

The epoxy composites (containing various percentages of lignin-based epoxy without fiberglass) were also characterized by dynamic mechanical analysis (DMA, Q800, TA Instruments). In the DMA measurements, the shear moduli were measured in oscillating bending at a frequency of 1 Hz and strain amplitude of 1% of the length of the sample heated from 30 ºC to 150 ºC at 5 ºC/min. Sample dimensions for the DMA tests were 60 mm×10 mm×2 mm. The average molar mass between crosslinks can be determined from DMA data by using Eq. (6-7) [2,33],

\[
M_c = \frac{\rho qRT}{G_e} \quad (6-7)
\]
where $M_c$ is the number average molar mass between crosslinks, $q$ is the front factor (usually equal to 1[34]), $\rho$ is the density at temperature $T$ (K), $G_e$ is the equilibrium modulus in the rubbery region at temperature $T$, and $R$ is the universal gas constant.

6.3 Results and Discussion

6.3.1 Dynamic DSC Data Analysis

The curing behaviors of the conventional BPA-based epoxy resin (DGEBA) and the epoxy composites comprising DGEBA and various percentages of lignin-based epoxy were investigated by dynamic DSC using DDM as the curing agent at four heating rates (i.e. 4, 6, 8 and 10ºC/min). The dynamic DSC thermographs of the conventional BPA-based epoxy (DGEBA), the epoxy resin composites comprising DGEBA and various percentages of DOL-epoxy, and the epoxy composites comprising DGEBA and various percentages of DKL-epoxy, are shown in Figures 6-2, 6-3 and 6-4, respectively. Tables 6-2 and 6-3 summarize some key curing properties such as the onset curing temperature ($T_{onset}$), the peak curing temperature ($T_p$) and the end-set curing temperature ($T_{end}$) for the conventional BPA-based epoxy resin and the epoxy composites comprising DGEBA and various percentages of lignin-based epoxy. The $T_{onset}$, $T_p$ and $T_{end}$ of each resin sample during its curing process is consistently higher with increasing the heating rate. This behavior can be attributed to this fact that at a higher heating rate the resin sample has less time at a specific temperature which retards the curing process [35]. However, the total heat of curing reactions remains constant for a specific resin sample, irrespective of the heating rates. The BPA-based epoxy has the highest value of the curing reaction heat (enthalpy) of around 289 J/g, followed by 180-236 J/g for the epoxy composites comprising DGEBA and various percentages of DOL-epoxy, and the epoxy composites comprising DGEBA and various percentages of DKL-epoxy has the lowest value of enthalpy (round 84-199 J/g). This behavior on the curing heat effects is believed to be attributed to the different epoxy contents (EC) of the epoxy resins tested. For instance, the DKL-based epoxy resins have the lowest amount of EC (= 5.6), compared with EC = 8.0 for the DOL-epoxy, while the DGEBA has the highest value of EC (= 14.6). With decreasing the overall epoxy content of an epoxy system, the total heat of reaction would decrease due to a smaller number of the reactive sites for the curing reactions. In addition, from Figures 6-3 and 6-4 and Table 6-3, the addition of a lignin-based epoxy resin (in particular the DKL-epoxy resin) to
DGEBA decreases its onset, peak and end-set curing temperatures likely because the presence of hydroxyl groups on the lignin-based epoxy resins could enhance the curing process via the etherification and homopolymerization reactions [36,37].

![DSC curves of the conventional BPA-based epoxy (DGEBA) at different heating rates.](image)

**Figure 6-2** DSC curves of the conventional BPA-based epoxy (DGEBA) at different heating rates.

**Table 6-2** Curing characteristics of the conventional BPA-based epoxy resin.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Heating rate (°C/min)</th>
<th>$T_{onset}$ (°C)</th>
<th>$T_{end}$ (°C)</th>
<th>$T_p$ (°C)</th>
<th>$\Delta H_{total}$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA-DDM</td>
<td>4</td>
<td>51.6</td>
<td>215.3</td>
<td>135.7</td>
<td>288.7</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>61.5</td>
<td>231.1</td>
<td>146.0</td>
<td>279.9</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>67.0</td>
<td>249.7</td>
<td>153.7</td>
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<td></td>
<td>10</td>
<td>76.8</td>
<td>260.4</td>
<td>160.2</td>
<td>289.9</td>
</tr>
</tbody>
</table>
Figure 6-3  DSC curves of epoxy composites comprising DGEBA and various percentages of DOL-epoxy at different heating rates.
Figure 6-4  DSC curves of epoxy composites comprising DGEBA and various percentages of DKL-epoxy at different heating rates.
Table 6-3 Curing characteristics of the epoxy composites comprising DGEBA and various percentages of lignin-based epoxy resins.

<table>
<thead>
<tr>
<th>Heating rate (°C/min)</th>
<th>ΔH_{total} (J/g)</th>
<th>T_{onset} (°C)</th>
<th>T_p (°C)</th>
<th>T_{end} (°C)</th>
<th>Heating rate (°C/min)</th>
<th>ΔH_{total} (J/g)</th>
<th>T_{onset} (°C)</th>
<th>T_p (°C)</th>
<th>T_{end} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>25% DOL-DDM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>50% DOL-DDM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>243.2</td>
<td>54.8</td>
<td>132.0</td>
<td>221.7</td>
<td>4</td>
<td>212.2</td>
<td>54.6</td>
<td>129.3</td>
<td>202.3</td>
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<td>239.8</td>
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<td>142.1</td>
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<td>155.7</td>
<td>271.6</td>
<td>10</td>
<td>203.8</td>
<td>69.0</td>
<td>151.1</td>
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<td><strong>75% DOL-DDM</strong></td>
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<td></td>
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<td><strong>100% DOL-DDM</strong></td>
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<tr>
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<td>189.7</td>
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<td>149.9</td>
<td>237.7</td>
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<td>180.1</td>
<td>54.4</td>
<td>150.0</td>
<td>240.0</td>
</tr>
<tr>
<td><strong>25% DKL-DDM</strong></td>
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<td></td>
<td></td>
<td></td>
<td><strong>50% DKL-DDM</strong></td>
<td></td>
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</tr>
<tr>
<td>4</td>
<td>198.7</td>
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<td>196.4</td>
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<td>40.8</td>
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<td>221.7</td>
</tr>
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</tr>
<tr>
<td><strong>75% DKL-DDM</strong></td>
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<td><strong>100% DKL-DDM</strong></td>
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<td>84.3</td>
<td>38.8</td>
<td>127.5</td>
<td>229.2</td>
</tr>
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</table>

6.3.2 Curing Kinetic Analysis

Elucidation of curing kinetics and mechanism can be helpful for seeking effective means to minimize the internal stress and produce a high performance finished product of thermosetting polymers [38–40]. In this work, the curing kinetics of lignin-based epoxy systems were evaluated by Kissinger method to obtain the overall activation energy, and the isoconversional Friedman method to determine the activation energy as a function of conversion (i.e., extent of the curing process). In Kissinger method, as explained previously in Eq. (6-3) the overall activation energy was calculated from the slope of the curve of ln(β/T_{p,i}^2) versus 1/T_p for the epoxy composites.
comprising DGEBA/DOL-epoxy and DGEBA/DKL-epoxy, as displayed in Figures 6-5 and 6-6, respectively. Table 6-4 presents the overall activation energies for curing of these two types of lignin-based epoxy composites with DDM. As presented in this Table, the overall activation energies of all resin systems are in a narrow range of 42-56 kJ/mol which is close to the reported value for the conventional petroleum-based epoxy systems cured by amine [37,40–42]. In general, the overall activation energy of epoxy composites containing DOL-epoxy is higher than that of an epoxy composite containing DKL-epoxy at the same percentage of blending. The overall activation energies of the 100% DGEBA and the 25% DOL-epoxy composite are almost the same (~ 48 kJ/mol). However, the activation energy of 25% DKL-epoxy composite and pure DKL epoxy is 45 kJ/mol and 42 kJ/mol, respectively, which are lower than that of the 100% DGEBA. The rest samples all have a higher activation energy in comparison with the conventional BPA-based epoxy resin. These results indicate that blending a lignin-based epoxy with conventional BPA-based epoxy at a low blending ratio (25 wt%) could promote the curing process likely via the presence of free hydroxyl groups on the structure of lignin-based epoxy resins. The hydroxyl content of DKL-epoxy resins is higher than that of DOL-epoxy resins, which account for a greater curing enhancement effect for the 25% DKL-epoxy composite (Table 6-4). Similar results were reported by Kong et al.[6] on the catalytic effects of lignin on the curing process of epoxy resin, likely because the presence of hydroxyl groups on the lignin-based epoxy resins could promote the curing process [36,37] as discussed previously in Figures 6-3 and 6-4.

However, further increasing the percentage of lignin-based epoxy in the epoxy composites to above 25 wt.%, do not decrease the overall activation energies as predicted but generally increase overall activation energies (Table 6-4). This is probably due to the fact that the viscosity of a resin composite system increases with increasing the amount of lignin-based epoxy resin, which compromises the promoting effects of the hydroxyl groups and retards the curing process. As an interesting finding, curing of the 75% DKL-epoxy composite gave the highest activation energy (55 kJ/mol), much higher than that of the 100% DKL-epoxy, suggesting some interaction occurring between the BPA-based epoxy and lignin-based epoxy while curing the bio-based epoxy resin composites if containing a high amount (i.e., 75 wt%) of lignin-based epoxy. For the bio-based epoxy composites containing DOL-epoxy, an increase in the percentage (0-100 wt%) of DOL-epoxy in the composites consistently increases the overall activation energy in curing of the
composites, suggesting that the negative effect of viscosity increase might dominate over the positive effect of the hydroxyl groups on the overall activation energy of the curing process.

**Figure 6-5** Plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ for the epoxy composites comprising DGEBA and various percentages of DOL-epoxy.

**Figure 6-6** Plots of $\ln(\beta/T_p^2)$ versus $1/T_p$ for the epoxy composites comprising DGEBA and various percentages of DKL-epoxy.
Table 6-4 Overall curing activation energies for all epoxy composites determined by Kissinger method.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA-DDM</td>
<td>48.4</td>
</tr>
<tr>
<td>25% DOL-DDM</td>
<td>48.3</td>
</tr>
<tr>
<td>50% DOL-DDM</td>
<td>51.9</td>
</tr>
<tr>
<td>75% DOL-DDM</td>
<td>50.8</td>
</tr>
<tr>
<td>100% DOL-DDM</td>
<td>52.4</td>
</tr>
<tr>
<td>25% DKL-DDM</td>
<td>45.1</td>
</tr>
<tr>
<td>50% DKL-DDM</td>
<td>50.8</td>
</tr>
<tr>
<td>75% DKL-DDM</td>
<td>55.5</td>
</tr>
<tr>
<td>100% DKL-DDM</td>
<td>42.4</td>
</tr>
</tbody>
</table>

In addition, the Friedman method was used to determine the actual activation energy during the curing process in the conversion range of 0.05-0.95. Figures 6-7 and 6-8 exhibit the variation of activation energy during the curing process for the lignin-based epoxy composites comprising various percentages of DOL-epoxy or DKL-epoxy, respectively. It is obvious that the amount of lignin-based epoxy resin in the epoxy composites has a significant effect on actual activation energy of epoxy composites suggesting changes in the curing reaction mechanism. It can be found that, in curing of 100% DGEBA and 25wt% DOL-epoxy composite as well as 25wt% DKL-epoxy composite follows the similar trend: all activation energies are <50 kJ/mol and generally decrease with increasing the extent of curing (conversion), suggesting that (1) the autocatalytic curing mechanism may be present in these resin systems [42–44], and (2) curing of bio-based epoxy composites comprising BPA-based epoxy and a low amount (25 wt%) of lignin-based epoxy is dominant by the curing behavior of the BPA-based epoxy. Although the hydroxyl groups in lignin-based epoxy could promote the curing process via the etherification and homopolymerization reactions [36,37], as discussed previously, the curing of bio-based epoxy composites comprising a higher amount (>25 wt%) of either DOL-epoxy or DKL-epoxy resulted in not only a much higher activation energy than that of 100% DGEBA but also a climbing trend of the activation energy vs. the degree of conversion during the whole curing process (except for the 100% DKL-epoxy which exhibited lower curing activation energies than those of the 100% DGEBA and any other bio-based epoxy composites at the initial curing stage α<~0.4). These results suggest that the negative effect of viscosity increase (causing reduced mobility of the curing agent in the resin system
might dominate over the positive effect of the hydroxyl groups on the actual activation energy in curing of the bio-based epoxy composites containing a higher amount (>25 wt%) of lignin-based epoxy.

**Figure 6-7**  Variation of activation energy vs. degree of conversion for the epoxy composites comprising DGEBA and various percentages of DOL-epoxy (Friedman method).

**Figure 6-8**  Variation of activation energy vs. degree of conversion for the epoxy composites comprising DGEBA and various percentages of DKL-epoxy (Friedman method).
6.3.3 Glass Transition Temperature ($T_g$)

The glass transition temperature ($T_g$) of the cured epoxy composites was measured by DSC based on the inflexion point of the stepwise transition. Figure 6-9 shows the $T_g$ of the cured epoxy composites comprising DGEBA and various percentages of DOL-epoxy or DKL-epoxy. The results demonstrate that the amount of lignin-based epoxy resin in the epoxy composites had a significant effect on $T_g$. $T_g$ of an epoxy composite comprising the DKL-epoxy resin was higher than that with the DOL-epoxy resin, which might be attributed to the greater hydroxyl content in the DKL-epoxy than that in the DOL-epoxy resin. The hydroxyl group in lignin-based epoxy could promote the curing process via the etherification and homopolymerization reactions [36,37], as discussed previously, leading to a higher cross-linking density of the cured resin samples, hence an increased $T_g$. The Figure also clearly shows that for both epoxy composite systems containing DOL-epoxy and DKL-epoxy, respectively, a common trend can be observed: the $T_g$ decreases with increasing the amount of lignin-based epoxy in the epoxy composites up to 50 wt.%, which could be explained by the lower epoxy content of lignin-based epoxy resins in contrast with the DGEBA, leading to a lower cross-link density in the bio-epoxy composites. Afterwards with further increasing the amount (>50 wt%) of lignin-based epoxy in the composites, the $T_g$ increases slightly for the DOL-epoxy containing composites, but drastically for the DKL-epoxy containing composites, which could be attributed to the greater hydroxyl content in the DKL-epoxy that could promote the curing process via the etherification and homopolymerization reactions [36,37], leading to a higher cross-linking density of the cured resin samples.
Figure 6-9  Glass transition temperature ($T_g$) of the cured epoxy composites comprising DGEBA and various percentages of DOL-epoxy or DKL-epoxy resins.

6.3.4 Mechanical Properties

The universal testing machine (UTM) was used in two modes to determine the tensile and flexural properties of bio-based epoxy composites. In tensile mode, Stress-strain relationship was obtained and the results for 25% DOL-DDM and 25% DKL-DDM are shown in Figure 6-10. Tensile stress was applied till the failure of the sample and the maximum applied stress prior to failure was recorded as the tensile strength and the slope of stress-strain plot determined modulus of elasticity. In flexural mode, load-displacement relationship was obtained and the results for 25% DOL-DDM and 25% DKL-DDM are shown in Figure 6-11. The flexural modulus ($E$) and flexural strength ($\sigma$) are defined by Equations (6-5) and (6-6), respectively.
Figure 6-10 Tensile results of the epoxy composites comprising DGEBA and 25 wt% of DOL-epoxy or DKL-epoxy.
Figure 6-11 Flexural results of the epoxy composites comprising DGEBA and 25 wt% of DOL-epoxy or DKL-epoxy.

The tensile and flexural properties of the fiber-reinforced plastics (FRPs) using bio-based epoxy resins comprising various amounts of lignin-based epoxy resins (0 -100 wt%) as matrices are illustrated in Figures 6-12 and 6-13, respectively. As shown in Figure 6-10, the tensile (flexural) strength of the FRP with 100% DGEBA-epoxy, 100% DKL-epoxy and 100% DOL-epoxy were measured as 214 MPa (260 MPa), 141 MPa (180 MPa) and 154 MPa (100 MPa), respectively. Thus, both the tensile and flexural strengths of the FRP with a pure lignin-based epoxy resin are much lower than those of the FRP with the conventional BPA-based epoxy, however the modulus of elasticity or the flexural modulus of the FRPs with pure lignin-based epoxy resins are all
comparable to those of the FRP with the conventional BPA-based epoxy. The FRPs prepared with bio-based epoxy resins comprising up to 50-75 wt% of lignin-based epoxy resins as matrices have better or comparable tensile and flexural strengths when compared with the FRP with 100% BPA-based epoxy resin. For modulus of elasticity and flexural modulus, the FRPs prepared with all bio-based epoxy resins comprising up to 100 wt% of lignin-based epoxy resins have better or comparable properties than the FRP with 100% BPA-based epoxy resin. These promising results showed that the lignin-based epoxy resin has great potential to be used as a substitute for petroleum-based epoxy resins in the manufacture of FRPs for structure and automobile applications that demand weight savings, precision engineering and finite tolerances.
Figure 6-12 Tensile strength and elastic modulus of the FRPs prepared with epoxy composites comprising DGEBA and various percentages of DOL-epoxy (a) or DKL-epoxy (b).
Figure 6-13 Flexural strength and flexural modulus of FRPs prepared with epoxy composites comprising DGEBA and various percentages of DOL-epoxy (a) or DKL-epoxy (b).

The mechanical properties of typical bulk bio-based epoxy composites (fully cured by DDM) were investigated further by DMA, the DMA profiles are displayed in Figure 6-14, where the storage modulus ($E'$) and $\tan\delta$ are plotted versus temperature. In addition, $T_g$ and the average molar mass between crosslinks ($M_c$) were obtained and are summarized in Table 6-5. The $T_g$ was determined by the peak temperature of $\tan\delta$ and the average molar mass between crosslinks were calculated from Eq. (6-7). The storage moduli of the two bio-based epoxy resins are both higher than that of the conventional BPA-based epoxy resin (BGEBA) at a low temperature ($<$50°C). The $T_g$ of BGEBA, 50%DOL-epoxy composite and 50%DKL-epoxy composite were determined from the
DMA measurement, and are presented in Table 6-5: 117°C, 83°C and 100°C, respectively. These results indicated that the obtained $T_g$’s from both DSC and DMA are in a very good agreement. Also, the calculated $M_c$ values for these resins are in a narrow range of 46-58 g/mol, suggesting similar cross-link densities, in a good agreement with their similar tensile and flexural properties.

Table 6-5 Glass transition temperature and crosslink density of 100% DGEBA and epoxy composites comprising DGEBA and 50 wt% of DOL-epoxy or DKL-epoxy.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
<th>$M_c$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DSC</td>
<td>DMA</td>
</tr>
<tr>
<td>DGEBA</td>
<td>129</td>
<td>117</td>
</tr>
<tr>
<td>50% DOL-DDM</td>
<td>85</td>
<td>83</td>
</tr>
<tr>
<td>50% DKL-DDM</td>
<td>101</td>
<td>100</td>
</tr>
</tbody>
</table>

6.4 Conclusions

In this study, lignin-based epoxy resin, prepared from de-polymerized kraft lignin (DKL) and de-polymerized organosolv lignin (DOL) were mixed with the conventional BPA-based epoxy resin
(BGEBA) at different percentages (0-100 wt%) to produce bio-based epoxy composites. The composites were cured with DDM, and the curing process was studied using DSC and the activation energy was calculated by Kissinger method and Friedman method. Fiber-reinforced plastics (FRPs) were prepared using the bio-based epoxy composites as polymer matrices and fiberglass mat. The mechanical properties (tensile and flexural strengths and modulus of elasticity and flexural modulus) of the FRPs were characterized by a UTM machine, and the mechanical properties of the bio-based epoxy composites were also investigated by DMA. Some major conclusions derived from this study are summarized as follows.

1. The BPA-based epoxy has the highest value of the curing reaction heat (enthalpy) of around 289 J/g, followed by DOL-based epoxy composites (180-236 J/g) and the DKL-based epoxy composites (round 84-199 J/g). This difference in the curing reaction enthalpy may be attributed to the different epoxy contents (EC) in the epoxy resins tested.

2. The addition of a lignin-based epoxy resin (in particular the DKL-epoxy) to the BPA-based epoxy decreases its onset, peak and end-set curing temperatures likely because the presence of hydroxyl groups on the lignin-based epoxy resins could promote the curing process.

3. Blending a lignin-based epoxy with conventional BPA-based epoxy at a low blending ratio (25 wt%) could promote the curing process likely via the presence of free hydroxyl groups on the structure of lignin-based epoxy resins. However, further increasing the percentage of lignin-based epoxy in the epoxy composite to above 25 wt.%, do not decrease the overall activation energies as predicted but generally increase overall activation energies. This is probably due to the fact that the viscosity of an epoxy composite system increases with increasing the amount of lignin-based epoxy, which compromises the promoting effects of the hydroxyl groups and hence retards the curing process.

4. The wt.% amount of lignin-based epoxy resin in the epoxy composites had a significant effect on $T_g$: $T_g$ decreases with increasing the amount of lignin-based epoxy in the resin composites up to 50 wt.%, and afterwards with further increasing the amount (>50 wt%) of lignin-based epoxy resins in the composites, the $T_g$ increases. $T_g$ of an epoxy composite comprising the DKL-based epoxy resin was higher than that with the DOL-based epoxy resin, which might be attributed to the greater hydroxyl content in the DKL-epoxy than that in the DOL-based epoxy resin.

5. The FRPs prepared with bio-based epoxy resins comprising up to 50-75 wt% of lignin-
based epoxy resins as matrices have better or comparable tensile and flexural strengths compared with the FRP with 100% BPA-based epoxy resin. For modulus of elasticity and flexural modulus, the FRPs prepared with all bio-based epoxy resins comprising up to 100 wt% of lignin-based epoxy resins have better or comparable properties than the FRP with 100% BPA-based epoxy resin.
6.5 References


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Simulation of Epoxy-Terminated Poly (phenylene ether ketone). III .Determination of the


Thermal Performance and Thermal Decomposition Kinetics of Lignin-Based Epoxy Resins
Abstract

Lignin-based epoxy resins derived from depolymerized kraft/organosolv lignins were blended with a commercial bisphenol A (BPA)-based epoxy resin at various percentages to prepare bio-based epoxy composites. The thermal stability and thermal decomposition kinetics of lignin-based epoxy composites were investigated using thermogravimetric analysis coupled with Fourier transformation infrared spectroscopy (TGA-FTIR) and compared with the conventional BPA-based epoxy resin. The activation energy of the decomposition process of the cured lignin-based epoxy composites was calculated by Kissinger, Kissinger-Akahira-Sunoe (KAS), and Flynn-Wall-Ozawa (FWO) methods. The presence of lignin-based epoxy resin demonstrated a significant effect on the activation energy of the decomposition process in particular at the early and the final stages of decomposition. The increase in the percentage of lignin-based epoxy resins in the composites reduced the initial activation energy of the system and increased the final activation energy of the system. Carbon oxides, methane, carbonyl compounds, amines and aromatic compounds were identified as the principal components during the thermal decomposition of the bio-based epoxy composites.
7.1 Introduction

Epoxy resins are one of the versatile thermosetting resins used in a wide variety of applications [1]. The thermal stability and fire-retardancy of epoxy resins play an important role in its final applications; particularly, when these resins are used in electronic industry [2] or in aerospace industry [3]. Therefore, the development of epoxy resins with high thermal stability has gained much interest in academia and industry.

Extensive research has been reported on thermal behavior of epoxy resins [3–6] and various approaches have been proposed to improve its thermal performance including the incorporation of aromatic rings and fire retarding additives into the epoxy cross-linked network [7–9] or co-polymerization of epoxy resins with reactive fire retardants [10,11]. The thermal stability and flammability of epoxy resins are strongly influenced by the chemical structure of the resins, the nature of curing agents used [5,6] and the crosslink density of the final products [5,12]. In general, the aromatic epoxy resins exhibit a higher thermal stability than the aliphatic one [3]. The influence of chemical structure of an epoxy resin on its thermal stability has been reported [4]. For instance, the tetragnecyldil-4,4'-diaminodiphenylmethane (TGDDM)-based epoxy resin has a higher thermal stability than the diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin [4]. Daykonov et al. [5] studied the effect of curing agents on the thermal stability of epoxy resin and found that for a given crosslink density, the thermal stability of resin with aromatic mono-amine curing agents is higher than that of the resin with corresponding aromatic diamine curing agents. In general, the thermal stability of a particular epoxy resin enhances with increasing its crosslink density [5]. Mustafa et al. [7] proposed a new pyridine-containing diamine as a curing agent which promoted the thermal stability of a tetra-epoxy resin compared to the traditional diamine curing agents.

Lignin is aromatic in nature and has several polar bonds (hydroxyl) which could interact with the cross-linked network of epoxy resin [13]. Therefore incorporation of lignin into the epoxy resin could improve the thermal stability of the composite. Lignin is considered as a thermal stabilizer of cellulose against thermal oxidation at low temperature [14]. Several investigations have been reported on the thermal stability of lignin [15–19]. It has a very complex structure and its thermal behavior depends on its nature and operating parameters such as temperature, pressure, heating rate and degradation atmosphere [20,21]. Lignin decomposes slowly in a wide range of temperature and it indicates the occurrence of several reactions at the same time [22,23]. Typically
decomposition of lignin shows a first weight-loss in the range of 100-180 °C due to the elimination of humidity. The second and third weight-loss peaks in the range of 280-390 °C and > 420 °C, respectively [20]. The kinetic parameters for thermal decomposition of lignin have been explored using the distributed activation energy model (DAEM) by several researchers [21,22].

Recently, several studies have been reported on the thermal stability of lignin-based epoxy resins [13,24,25]. The thermal properties of epoxy resins cured with various percentages of aminated lignin and W39 amine curing agent demonstrated that with increasing the content of aminated lignin (from 20% to 100%), the temperature at 10% weight loss ($T_{10}$) increased towards high temperature end. The cured sample with W39 curing agent had a low $T_{10}$ and its total mass loss before 300 °C was 11.1% which was the highest among other samples [13]. Sasaki et al. [26] reported the thermal stability of a cured bamboo lignin-based epoxy resin (BL-epoxy) with two different curing agents. The results indicated that the thermal stability of both bio-based epoxy systems met the minimum requirements for using as solder-dip resistance (250-280°C) in printed circuit board. The kinetics of the thermal decomposition of epoxy resins have also been reported in literature[27,28].

The main objective of this work was focused on the thermal behavior of bio-based epoxy composites comprising the BPA-based epoxy resin and 25-100 wt% of the lignin-based epoxy resins derived from de-polymerized kraft/organosolv lignins. The thermal stability of bio-based epoxy composites was investigated by thermogravimetric analysis (TGA) and the decomposition kinetics were studied using model-free kinetic methods such as Kissinger-Akahira-Sunoe (KAS) and Flynn-Wall-Ozawa (FWO) to determine the activation energy. In addition, TGA-FTIR was used to characterize the gases produced during the decomposition process of bio-based epoxy composites, which helps elucidate the dominant mechanism of thermal decomposition of the bio-based epoxy composites.

7.2 Experimental

7.2.1 Materials

Lignin-based epoxy resins were synthesized from de-polymerized kraft lignin (DKL, softwood) and de-polymerized organosolv lignin (DOL, hardwood), and hereafter will be referred as DKL-epoxy resin and DOL-epoxy resin, respectively. The detailed synthesis procedure of the lignin-
based epoxy resins has been discussed in the previous chapters and in our published papers [29,30]. Araldite (grade: GZ 540 X 90, DGEBA), a conventional bisphenol A (BPA)-based epoxy resin with an epoxide equivalent weight (EEW) of 295 g/eq was supplied by Huntsman and used in this study to prepare bio-based epoxy composites. 4,4’-Diaminodiphenylmethane (DDM) was purchased from Sigma Aldrich and used as a curing agent for the epoxy resins or composites.

### 7.2.2 Sample Preparation

Bio-based epoxy composites were prepared by mixing the conventional BPA-based epoxy resin (DGEBA) and a desired amount of lignin-based epoxy resins (DKL-epoxy resin or DOL-epoxy resin) at 80 °C. The curing agent, DDM, was added into the mixture based on the specifications given in Table 7-1. The epoxy composites were placed in a pre-heated oven based on the curing conditions as determined in our previous work (Chapter 5). Typically, the epoxy composites were cured at its peak curing temperature \(T_p\) for 4 h and post-cured at the end curing temperature \(T_{end}\) for 90 min. The cured bio-based epoxy composites were all crushed into fine particles for further analysis. The sample names with specifications are shown in Table 7-1.

**Table 7-1** Sample names with specifications.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>DGEBA (g)</th>
<th>DOL-based epoxy resin (g)</th>
<th>DKL-based epoxy resin (g)</th>
<th>DDM (g)(^1)</th>
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</thead>
<tbody>
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<td>DGEBA-DDM</td>
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<td>0</td>
<td>0</td>
<td>16.8</td>
</tr>
<tr>
<td>25% DKL-DDM</td>
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<td>50</td>
<td>11.7</td>
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<tr>
<td>75% DKL-DDM</td>
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<td>75</td>
<td>9.1</td>
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<td>6.5</td>
</tr>
<tr>
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<td>25</td>
<td>0</td>
<td>14.9</td>
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<tr>
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<td>0</td>
<td>13</td>
</tr>
<tr>
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<td>75</td>
<td>0</td>
<td>11.1</td>
</tr>
<tr>
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<td>0</td>
<td>100</td>
<td>0</td>
<td>9.2</td>
</tr>
</tbody>
</table>

\(^1\) Based on the stoichiometric ratio of amine group in the curing agent to the epoxy group in the epoxy resin.

### 7.2.3 Characterization

The TGA-FTIR analysis was conducted on a thermogravimetric analysis (TGA, Perkin Elmer Pyris 1 TGA unit), coupled with a Fourier transform infrared spectrometry. The coupling line (Perkin-Elmer’s TL 8000 transfer line) between the TGA and FTIR was heated at 300°C to pass
all evolved vapor (without condensation). The dynamic TGA experiments were performed on the cured epoxy composites at various heating rates of 5, 10, 15 and 20 °C/min over a temperature range of 50 °C to 800 °C under a constant flow of nitrogen of 20 ml/min. TGA-FTIR was used to identify the gaseous components generated during the thermal decomposition of DGEBA-DDM, 100%DKL-DDM and 100%DOL-DDM composites at a ramp rate of 40 °C/min. The FTIR absorbance spectra were in the range of 4000-500 cm⁻¹.

The average molecular weights and polydispersity index of the lignin-based epoxy resins were characterized using a Waters Breeze GPC-HPLC instrument (1525 binary lamp, UV detector set at 270 nm, Waters Styragel HR1 column at 40°C) using THF as the eluent at a flow rate of 1 ml/min with linear polystyrene standards for building the molecular weight calibration curve.

### 7.2.4 Model Free Kinetics

Thermal decomposition of a cured epoxy resin is a solid state reaction [4,23]. In general, the rate of thermal decomposition can be expressed as a function of degree of conversion \( f(\alpha) \), and temperature \( k(T) \) as shown in Eq. (7-1) [31].

\[
\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = f(\alpha)k(T) \tag{7-1}
\]

where, \( \beta \) is the linear heating rate (°C/min) and \( \alpha \) is the mass loss fraction which can be defined by the Eq. (7-2) [23,32]. The temperature dependency of \( k(T) \) can be explained by the Arrhenius expression (Eq. (7-3)):

\[
\alpha = \frac{M_0 - M_T}{M_0 - M_\infty} \tag{7-2}
\]

where \( M_0 \) is the initial mass of sample, \( M_T \) is the mass of sample residue at temperature, \( T \) during the thermal decomposition and \( M_\infty \) is the final mass residue of the sample when the experiment is completed.

\[
k(T) = A \exp\left(-\frac{E}{RT}\right) \tag{7-3}
\]

where \( A \) is the pre-exponential factor, \( R \) is the gas constant and \( E \) is the activation energy. By inserting Eq. (7-3) in Eq. (7-1) and integrating by separation of variables, Eq. (7-4) can be obtained [31,33].
where $G(\alpha)$ is the integral form of $f(\alpha)$, $u$ is $E/RT$ and $P(u)$ is generally defined as a temperature integral. There are various mathematical assumptions for $P(u)$ to determine the activation energy. An integral method to obtain the overall activation energy of the thermal decomposition process is the Kissinger method which can be given as [27,34].

$$\ln\left(\frac{\beta}{T_{\text{max}}^2}\right) = \text{Cons.} - \frac{E}{RT_{\text{max}}}$$  \hspace{1cm} (7-5)

where $T_{\text{max}}$ is the temperature at which the maximum rate of the thermal decomposition takes place.

Two different isoconversional methods, namely Kissinger-Akahira-Sunoe (KAS) method [35] and Flynn-Wall-Ozawa (FWO) method [4,27], are also used to define the activation energy of the thermal decomposition as a function of conversion. The KAS and FWO methods are shown in Eqs. (7-6) and (7-7), respectively.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln \frac{AR}{EG(\alpha)} - \frac{E}{RT}$$  \hspace{1cm} (7-6)

$$\log \beta = \log \frac{AE}{RG(\alpha)} - 2.315 - 0.4567 \frac{E}{RT}$$  \hspace{1cm} (7-7)

According to the KAS and FWO methods, the activation energy for a specific value of $\alpha$ can be obtained from the slopes of plot $\ln(\beta/T^2)$ vs. $1/T$ and plot $\log(\beta)$ vs. $1/T$, respectively for a set of 4 heating rates ($\beta$). It should be noted that $T$ is strongly dependent on $\beta$ at a specific value of $\alpha$, as discussed previously.

### 7.3 Results & Discussion

#### 7.3.1 TGA Analysis of Epoxy Composites

The dynamic TG and DTG thermographs of the conventional BPA-based epoxy resin (DGEBA), the bio-based epoxy composites comprising DGEBA and various percentages of DKL-epoxy and the epoxy composites comprising DGEBA and various percentages of DOL-epoxy at different heating rates are shown in Figures 7-1, 7-2 and 7-3, respectively. As observed in these Figures, the maximum rate decomposition temperature ($T_{\text{max}}$) of all the samples shifts towards a high
temperature when increasing the heating rate. This behavior can be attributed to the heat and mass transfer limit in sample which lead to a difference in temperature between the sample and the reference (causing the actual temperature of the sample lower than the reference temperature upon a higher heating rate) [23]. The thermal decomposition of the conventional BPA-based epoxy resin exhibited a single decomposition step in the range of 350-500 ºC with the maximum rate of decomposition at around 405 ºC and a small shoulder at a higher temperature. The maximum rate of decomposition of DGEBA-DDM is in a good agreement with the values reported for typical epoxy resins in literature [4,36]. An obvious difference is observed between the thermal decomposition of 100% DKL-DDM and 75% DKL-DDM with other epoxy composites. The epoxy composites containing high quantity of DKL-epoxy resin (100% and 75%) have two significant weight-loss peaks in their DTG curves. The first weight loss at 250-400 ºC which is mainly related to the decomposition of small molecular weight fractions and the later main peak at 400-500 ºC is due to the decomposition of macromolecules. Based on the GPC results, DKL-epoxy resin has a wide range of molecular weight, its average molecular weight ($M_w$) was 2800g/mol and its polydispersity index (PDI) was 3.5. The small molecules can show a low thermal stability and decompose at a relatively lower temperature. With increasing the percentages of DKL-epoxy (25-100 wt.%) in the epoxy composites, the homogeneity of the epoxy composites decreases and the decomposition peak gradually broadened and in some cases (75% and 100% DKL-epoxy) two distinct peaks are observed. This could be attributed to the degradation of different linkages present in lignin. In contrast to the DKL-based epoxy composites, the DOL-based epoxy composites exhibited a single decomposition step in the range of 350-450 ºC with the maximum rate of decomposition at around 400 ºC, suggesting the DOL-based epoxy composites are less thermally stable than the conventional BPA-based epoxy resin and the DKL-based epoxy composites. DOL-epoxy resin has a low $M_w$ (=1400 g/mol) with a narrow polydispersity index (=2.8). As a result, the weight loss of the DOL-based epoxy composites would occur at a relatively lower temperature in compared to the DKL-based epoxy composites with narrow decomposition peaks.
Figure 7-1 TG and DTG curves of the conventional BPA-based epoxy (DGEBA) at different heating rates.
Figure 7-2 TG and DTG curves of epoxy composites comprising DGEBA and various percentages of DKL-epoxy at different heating rates.
Figure 7-3 TG and DTG curves of epoxy composites comprising DGEBA and various percentages of DOL-epoxy at different heating rates.
Table 7-2 presents some key thermal properties such as initial decomposition temperature (IDT), maximum rate decomposition temperature (\(T_{\text{max}}\)), char yield at 800 °C and limiting oxygen index (LOI) for the conventional BPA-based epoxy resin and the epoxy composites comprising DGEBA and various percentages of lignin-based epoxy at 10 °C/min heating rate. LOI is the minimum amount of oxygen required to continue the combustion of materials. It is a parameter to measure the flammability of the polymeric materials and determines the effectiveness of fire retardants [37]. LOI can be calculated on the basis of the char residue (CR) by applying Van Krevelen and Hoftyzer method (Eq. (7-8)) [7,36]. Materials with LOI below 20.95% can easily burn in air and materials with LOI above 28 are considered as “self extinguishing” materials [37].

\[
LOI = 17.5 + 0.4CR 
\]  
\(7-8\)

As shown in Table 7-2, the thermal decomposition of the conventional BPA-based epoxy resin starts at 370 °C and the maximum rate of decomposition is at 405 °C. The incorporation of lignin-based epoxy resin (in particular the DKL-epoxy resin) to DGEBA reduces the initial decomposition temperature (IDT) likely due to the presence of low M_w lignin components and the lignin-based epoxy resins. It is worth mentioning that all lignin-based epoxy resins meet the minimum thermal stability (250-280 °C) which is required for the application in the electronic field [26].

The maximum decomposition temperature of the conventional BPA-based epoxy resin is around 405 °C. The addition of DOL-epoxy resin and a low amount of DKL-epoxy resin (<50%), the \(T_{\text{max}}\) is almost stable in the range of 397-404 °C, very similar to the value of the BPA-based epoxy resin. The \(T_{\text{max}}\) of the 100% and 75% DKL-DDM system (416 and 407 °C, respectively) is even higher than that of the conventional epoxy resin, suggesting better thermal stability of these bio-based epoxy composites. With the incorporation of lignin-based epoxy resins, the mass residue at 800 °C increase for both lignin-based epoxy systems. Furthermore, the limiting oxygen index (LOI) of all lignin-based epoxy composites is higher than that of the conventional BPA-based epoxy resin indicating that the lignin-based epoxy resins are more effective fire retardants than DGEBA system. Particularly, the highest value is related to 100% DKL-DDM system. Based on the above definition, 75% DKL-DDM, 100% DKL-DDM and 100% DOL-DDM can be classified as the self-extinguishing materials.
Table 7-2 Thermal decomposition data of the conventional BPA-based epoxy resin and the epoxy composites comprising DGEBA and various percentages of lignin-based epoxy resins at 10ºC/min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>IDT(ºC)</th>
<th>Shoulder Peak</th>
<th>Main Peak</th>
<th>Char800 (%)</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>DGEBA-DDM</td>
<td>370</td>
<td>-</td>
<td>405</td>
<td>12.5</td>
<td>22.5</td>
</tr>
<tr>
<td>25% DKL-DDM</td>
<td>359</td>
<td>-</td>
<td>397</td>
<td>18</td>
<td>24.7</td>
</tr>
<tr>
<td>50% DKL-DDM</td>
<td>330</td>
<td>-</td>
<td>396</td>
<td>25</td>
<td>27.5</td>
</tr>
<tr>
<td>75% DKL-DDM</td>
<td>300</td>
<td>335</td>
<td>407</td>
<td>32</td>
<td>30.3</td>
</tr>
<tr>
<td>100% DKL-DDM</td>
<td>290</td>
<td>325</td>
<td>416</td>
<td>38</td>
<td>32.7</td>
</tr>
<tr>
<td>25% DOL-DDM</td>
<td>383</td>
<td>-</td>
<td>404</td>
<td>17</td>
<td>24.3</td>
</tr>
<tr>
<td>50% DOL-DDM</td>
<td>352</td>
<td>-</td>
<td>399</td>
<td>21</td>
<td>25.9</td>
</tr>
<tr>
<td>75% DOL-DDM</td>
<td>338</td>
<td>-</td>
<td>398</td>
<td>24</td>
<td>26.7</td>
</tr>
<tr>
<td>100% DOL-DDM</td>
<td>335</td>
<td>-</td>
<td>397</td>
<td>29</td>
<td>29.1</td>
</tr>
</tbody>
</table>

7.3.2 TGA-FTIR Analysis

The coupled TGA-FTIR analyzer was used to study the mechanism of the thermal decomposition of pure lignin-based epoxy resins, compared with the BPA-based epoxy resin (DGEBA). For TGA-FTIR analysis, the samples were heated purposely at a high heating rate (i.e., 40 ºC/min) to generate enough gases from the decomposition process to enable the FTIR analyzer create a clear spectrum for detecting the released gases. Figure 7-4 illustrates the TG/DTG profiles of DGEBA-DDM, 100% DKL-DDM and 100% DOL-DDM. The 3D-FTIR results of the entire decomposition process and the FTIR spectra at $T_{max}$ are displayed in Figure 7-5. There is a good agreement between the weight-loss from TGA results and the absorbance peaks of FTIR for all samples. The 3D FTIR of 100% DKL-DDM exhibits two distinct peaks as well as its DTG results. A wide range of volatile components evolved during the thermal degradation of epoxy composites and the corresponding absorbance are summarized in Table 7-3. The DGEBA-DDM exhibits a single decomposition step with $T_{max}$ at 426 ºC. The main volatile components were identified as CO$_2$ (2360, 668cm$^{-1}$), CO (2180cm$^{-1}$), CH$_4$ (2800cm$^{-1}$), H$_2$O (3570cm$^{-1}$), amine (3450cm$^{-1}$), carbonyl components (1730 cm$^{-1}$) and aromatic components (1508cm$^{-1}$). As the epoxy resins cured with the amine component, the N-containing species are also detected in FTIR spectra. CH$_4$, CO$_2$ and CO are mainly generated from the cleavage of functional groups such as ether groups, methoxy, methyl and methylene groups at high temperatures [38]. The evolution of gases of the conventional BPA-
based epoxy resin are in a good agreement with those of the typical epoxy resins reported by other researchers [39–41].

The thermal decomposition of the 100% DKL-DDM sample exhibits two decomposition steps. The first step occurs at 351°C where the main evolved gases are CO₂, H₂O and CH₄. The emission of CO₂ could be associated with the decarboxylation reaction and the cleavage of carbonyl, carboxyl and carbonyl ester groups present in the side chains of the phenylpropane units of lignin [16,18,23]. The generation of H₂O could be from the cracking of aliphatic and aromatic hydroxyl groups [16]. CH₄ might be released from the demethylation of methoxy groups and rupture of methoxy, methyl and methylene groups [16,23]. The second decomposition step takes place at 433°C where more gaseous components are evolved than the first step. The predominant fragments are CO₂, H₂O and CH₄, carbonyl components (carboxylic acids, aldehydes, 1600-1800 cm⁻¹) and aromatic components (1500 cm⁻¹). Carboxylic acids and aldehydes could be formed from the cleavage of aliphatic side-chains [15,38]. The formation of aromatic fragments could be associated with the decomposition of the typical ether linkages of the phenyl-propanols in the lignin structure [38].

A single decomposition step was observed for 100% DOL-DDM system at 413 °C. CO₂, CO, CH₄, H₂O, amine, carbonyl components and aromatic components were mainly generated at this temperature. The mechanism for the formation of these gaseous components is similar to DKL-based epoxy system.
Figure 7-4 TG and DTG profiles of 100% DGEBA, 100% DKL-based epoxy and 100% DOL-based epoxy heated in N₂ at 40°C/min.
Figure 7-5 FTIR diagrams of the evolved vapors from 100% DGEBA, 100% DKL-based epoxy and 100% DOL-based epoxy during the TGA tests: (a) 3D FTIR diagram (b) FTIR spectrum for volatiles at $T_{\text{max}}$. 

100% DKL-DDM

100% DOL-DDM
### Table 7-3 Assigned absorbance bands of the volatile components.

<table>
<thead>
<tr>
<th>Components</th>
<th>Functional Groups</th>
<th>Absorbance range (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>C-H</td>
<td>3000-2700</td>
</tr>
<tr>
<td>CO</td>
<td>C=O</td>
<td>2250-2000</td>
</tr>
<tr>
<td>CO₂</td>
<td>C=O, Stretching</td>
<td>2400-2250</td>
</tr>
<tr>
<td>CO₂</td>
<td>C=O, Bending</td>
<td>730-580</td>
</tr>
<tr>
<td>H₂O</td>
<td>O-H</td>
<td>4000-3400</td>
</tr>
<tr>
<td>Amine</td>
<td>N-H, Stretching</td>
<td>3500-3300</td>
</tr>
<tr>
<td>Amine</td>
<td>N-H, Bending</td>
<td>1640-1560</td>
</tr>
<tr>
<td>Amine</td>
<td>C-N</td>
<td>1350-1000</td>
</tr>
<tr>
<td>Aromatics</td>
<td>C=C</td>
<td>1690-1450</td>
</tr>
<tr>
<td>Alkanes, phenols, ethers, alcohols</td>
<td>C-O, C-C</td>
<td>1480-1000</td>
</tr>
<tr>
<td>Aldehydes, ketones, acids</td>
<td>C=O</td>
<td>1900-1650</td>
</tr>
</tbody>
</table>

#### 7.3.3 Kinetics Analysis

Activation energy ($E$) of the thermal decomposition process can be used as a criteria for comparing the thermal stability of polymers [36]. In order to investigate the thermal stability of lignin-based epoxy composites, the activation energy was determined on the basis of three different model free kinetics, namely Kissinger, KAS, and FWO methods.

The overall activation energy of the conventional BPA-based epoxy resin (DGEBA), the bio-based epoxy composites comprising DGEBA and various percentages of DKL-epoxy and the bio-based epoxy composites comprising DGEBA and various percentages of DOL-epoxy was calculated on the basis of Kissinger method and the obtained results are displayed in Table 7-4. In Kissinger method, the overall activation energy determines based on the $T_{\text{max}}$. As the DTG profiles of 75% DKL-DDM and 100% DKL-DDM systems demonstrated two $T_{\text{max}}$, two overall activation energies were reported for these systems. In general, most of the bio-based epoxy composites have a higher activation energy than the BPA-based epoxy resin, and the DOL-based epoxy composites have higher activation energy in compared to that of the DKL-based epoxy composites. The highest activation energy (212 kJ/mol) is obtained for 25% DOL-DDM system. Thus, the thermal stability of the bio-based epoxy resin composites, in particular the DOL-based epoxy composites have better thermal stability, if simply based on the overall activation energy. However, the
decomposition of the lignin-based epoxy composites is a very complex process with multiple reactions taking place simultaneously. Therefore, a single activation energy is unable to explain the entire process and would be better to use isoconversional methods to calculate the activation energy as a function of conversion ($\alpha$).

Table 7-4 Overall activation energies of the thermal decomposition for all epoxy resin composites determined by Kissinger method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kissinger Method, E(kJ/mol) ($R^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shoulder Peak</td>
</tr>
<tr>
<td>DGEBA-DDM</td>
<td>-</td>
</tr>
<tr>
<td>25%DKL-DDM</td>
<td>-</td>
</tr>
<tr>
<td>50%DKL-DDM</td>
<td>-</td>
</tr>
<tr>
<td>75%DKL-DDM</td>
<td>125 (0.98)</td>
</tr>
<tr>
<td>100%DKL-DDM</td>
<td>111 (0.99)</td>
</tr>
<tr>
<td>25%DOL-DDM</td>
<td>-</td>
</tr>
<tr>
<td>50%DOL-DDM</td>
<td>-</td>
</tr>
<tr>
<td>75%DOL-DDM</td>
<td>-</td>
</tr>
<tr>
<td>100%DOL-DDM</td>
<td>-</td>
</tr>
</tbody>
</table>

Tables 7-5 and 7-6 show the activation energy based on model free kinetics and the value of correlation coefficient ($R^2$) for the bio-based epoxy composites comprising DGEBA and various percentages of DKL-epoxy and the bio-based epoxy composites comprising DGEBA and various percentages of DOL-epoxy systems, respectively. As shown in these Tables, all the points exhibit a good correlation coefficient for both KAS and FWO methods. Both methods demonstrated a similar trend for the distribution of activation energy with an insignificant difference in the activation energy values. This indicates an excellent agreement of the results obtained from both methods and proved the accuracy and reliability of the estimated values.

Figures 7-6 and 7-7 illustrate the distribution of activation energy during the thermal decomposition process for the lignin-based epoxy composites comprising various percentages of DKL-epoxy resin or DOL-epoxy resins, respectively. It is obvious that the activation energy of all epoxy composites depends on the extent of conversion. The thermal decomposition of the conventional BPA-based epoxy resins and the lignin-based epoxy composites is a complex process.
with several parallel, competitive and consecutive reactions. Lignin-based composites can be de-polymerized to evolve light components including CO$_2$, CO, H$_2$O, as evidenced by the TGA-FTIR measurements (Figure 7-5), via reactions with low activation energy and decomposed to monomers via reactions with high activation energy [20,23].

The general pattern of the dependency of activation energy on the extent of conversion is strikingly similar for all epoxy composites through the decomposition process. For DGEBA-DDM, the activation energy increased slightly in the range of 136 kJ/mol - 163 kJ/mol up to 70% extent of decomposition and increased dramatically after that up to 245 kJ/mol, likely because partially cured (cross-linked) resin molecules become more rigid, thus limiting the self-curing reactions and raising the decomposition activation energy due to the rigidity. Similar results have been reported in literature for the thermal decomposition of epoxy resins [4,5,27].

As expected, the DKL-based epoxy composites have lower activation energies at the beginning of the decomposition process (< 35% mass-loss) compared to the DGEBA-DDM. With increasing the content of DKL-epoxy resin in the bio-based epoxy composites from 25% to 100%, a reduction in the activation energy from 112 kJ/mol to 60 kJ/mol for KAS method (or from 116 kJ/mol to 65 kJ/mol for FWO method) was observed at the early stage of the decomposition. A similar trend of variation in the activation energy is also observed for the DOL-based epoxy composites (except 25%DOL-DDM sample) which have lower activation energy in comparison with DGEBA-DDM at low values of conversion ($\alpha < 0.3$). For instance, with DOL-based epoxy composites the activation energy reduces from 131 kJ/mol to 77 kJ/mol for KAS method for the 50-100%DOL-DDM samples at the early stages of decomposition ($\alpha < 0.3$). The lower activation energy of bio-based epoxy composites at $\alpha < 0.3$ indicates a high reaction rate with low thermal stability compared with the BPA-based epoxy system. This behavior can be attributed to the cleavage of the weak bonds such as C-O bands on $\beta$-O-4’ structure, aryl-ethers bonds and the side chains on the structure of lignin including methoxy, hydroxy, carbonyl and carboxy bonds [20,23,42]. The activation energy for these weak bonds were estimated to be 70.68 kJ/mol [43], 33.2 kJ/mol [44] and 54.34 kJ/mol, respectively [20]. The interaction of epoxy resin and lignin increases the activation energy in this stage compared to the single component of lignin.

For the second stage of the decomposition process, $0.30 < \alpha < 0.75$, the activation energies of all lignin-based epoxy composites are almost the same as those of the conventional BPA-based epoxy
resin and increases slightly from 150 kJ/mol to 180 kJ/mol. In this stage, the main degradation may be related to the deformation of C-C and β-β linkages and the random scission on the crosslink of epoxy resins and lignin [20,23]. This degradation leads to the generation of the polymeric matrix with a low degree of polymerization with a short chain length.

At the final stage, 0.75 < α < 0.95, the general trend of the variation of activation energy is similar for all epoxy composites. The activation energy of the conventional BPA-based epoxy resin increases dramatically from 163 kJ/mol to 245 kJ/mol. While the increase in the activation energy of the lignin-based epoxy composites depends on the percentages of lignin-based epoxy resins. With increasing the percentages of lignin-based epoxy resin in composites from 0 to 100%, the final activation energy increases from 298 kJ/mol to 541 kJ/mol for DKL-based epoxy composites and from 283 kJ/mol to 561 kJ/mol for DOL-based epoxy composites. In this stage, the degradation process involves the cleavage and the rearrangement of stronger bonds in aromatic rings [20] and the rupture of 3-dimensional network of lignin and epoxy resins [23], thus requiring large activation energies.

Figure 7-6 Variation of activation energy vs. degree of conversion for the epoxy composites comprising DGEBA and various percentages of DKL-epoxy (KAS method).
Figure 7-7 Variation of activation energy vs. degree of conversion for the epoxy composites comprising DGEBA and various percentages of DOL-epoxy (KAS method).
Table 7-5 Variation of activation energy for the conventional BPA-epoxy (DGEBA) and the bio-based epoxy composites comprising DGEBA and various percentages of DKL-epoxy from $\alpha = 0.05$ to $\alpha = 0.95$ (KAS and FWO methods).

<table>
<thead>
<tr>
<th>Conversion (%)</th>
<th>DGEBA-DDM</th>
<th>DKL-Based Epoxy Resin-DDM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KAS ($R^2$)</td>
<td>FWO ($R^2$)</td>
</tr>
<tr>
<td>5</td>
<td>135.8 (0.96)</td>
<td>149.4 (0.98)</td>
</tr>
<tr>
<td>10</td>
<td>149.4 (0.98)</td>
<td>150.9 (0.99)</td>
</tr>
<tr>
<td>15</td>
<td>150.9 (0.99)</td>
<td>153.7 (0.99)</td>
</tr>
<tr>
<td>20</td>
<td>153.7 (0.99)</td>
<td>162.6 (0.99)</td>
</tr>
<tr>
<td>25</td>
<td>162.6 (0.99)</td>
<td>164.4 (0.99)</td>
</tr>
<tr>
<td>30</td>
<td>164.4 (0.99)</td>
<td>166.8 (0.99)</td>
</tr>
<tr>
<td>35</td>
<td>166.8 (0.99)</td>
<td>167.7 (0.99)</td>
</tr>
<tr>
<td>40</td>
<td>167.7 (0.99)</td>
<td>168.4 (0.99)</td>
</tr>
<tr>
<td>45</td>
<td>168.4 (0.99)</td>
<td>167.7 (0.99)</td>
</tr>
<tr>
<td>50</td>
<td>167.7 (0.99)</td>
<td>168.4 (0.99)</td>
</tr>
<tr>
<td>55</td>
<td>168.4 (0.99)</td>
<td>167.7 (0.99)</td>
</tr>
<tr>
<td>60</td>
<td>167.7 (0.99)</td>
<td>168.4 (0.99)</td>
</tr>
<tr>
<td>65</td>
<td>168.4 (0.99)</td>
<td>167.7 (0.99)</td>
</tr>
<tr>
<td>70</td>
<td>167.7 (0.99)</td>
<td>168.4 (0.99)</td>
</tr>
<tr>
<td>75</td>
<td>168.4 (0.99)</td>
<td>167.7 (0.99)</td>
</tr>
<tr>
<td>80</td>
<td>167.7 (0.99)</td>
<td>168.4 (0.99)</td>
</tr>
<tr>
<td>85</td>
<td>168.4 (0.99)</td>
<td>167.7 (0.99)</td>
</tr>
<tr>
<td>90</td>
<td>167.7 (0.99)</td>
<td>168.4 (0.99)</td>
</tr>
<tr>
<td>95</td>
<td>168.4 (0.99)</td>
<td>167.7 (0.99)</td>
</tr>
</tbody>
</table>
Table 7-6 Variation of activation energy for the epoxy composites comprising DGEBA and various percentages of DOL-epoxy from $\alpha = 0.05$ to $\alpha = 0.95$ (KAS and FWO methods).

<table>
<thead>
<tr>
<th>Conversion (%)</th>
<th>DOL-Based Epoxy Resin-DDM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 wt%</td>
</tr>
<tr>
<td></td>
<td>KAS ($R^2$)</td>
</tr>
<tr>
<td>5</td>
<td>163.4 (0.97)</td>
</tr>
<tr>
<td>10</td>
<td>156.8 (0.96)</td>
</tr>
<tr>
<td>15</td>
<td>156.9 (0.99)</td>
</tr>
<tr>
<td>20</td>
<td>157.7 (0.97)</td>
</tr>
<tr>
<td>25</td>
<td>166.8 (0.99)</td>
</tr>
<tr>
<td>30</td>
<td>167.4 (0.99)</td>
</tr>
<tr>
<td>35</td>
<td>171.4 (0.99)</td>
</tr>
<tr>
<td>40</td>
<td>172.2 (0.99)</td>
</tr>
<tr>
<td>45</td>
<td>174.7 (0.99)</td>
</tr>
<tr>
<td>50</td>
<td>178 (0.99)</td>
</tr>
<tr>
<td>55</td>
<td>177.3 (0.99)</td>
</tr>
<tr>
<td>60</td>
<td>179.2 (0.99)</td>
</tr>
<tr>
<td>65</td>
<td>181.4 (0.99)</td>
</tr>
<tr>
<td>70</td>
<td>183.7 (0.99)</td>
</tr>
<tr>
<td>75</td>
<td>185.7 (0.98)</td>
</tr>
<tr>
<td>80</td>
<td>187.6 (0.97)</td>
</tr>
<tr>
<td>85</td>
<td>224.7 (0.94)</td>
</tr>
<tr>
<td>90</td>
<td>266.7 (0.87)</td>
</tr>
<tr>
<td>95</td>
<td>283.5 (0.90)</td>
</tr>
</tbody>
</table>
7.4 Conclusions

In this study, lignin-based epoxy resin, prepared from de-polymerized kraft lignin (DKL) and de-polymerized organosolv lignin (DOL) were mixed with the conventional BPA-based epoxy resin (DGEBA) to produce lignin-based epoxy composites. DDM was used as a curing agent in process. The thermal stability of the prepared lignin-based epoxy composites was studied using TGA and the activation energy of the decomposition process was calculated by KAS and FWO methods. In addition, the evolved gases were analyzed in-situ with a coupled TGA-FTIR analyzer to elucidate the possible mechanism of decomposition of the resins or composites during the thermal degradation process. Some major conclusions derived from this study are summarized as follows.

1. With increasing the percentages of DKL-epoxy (25-100 wt%) in the epoxy composites, the homogeneity of the epoxy composites decreases and the thermal decomposition peak gradually broadens and for the epoxy composites comprising 75% DKL-epoxy and 100% DKL-epoxy two distinct peaks were observed.

2. The addition a lignin-based epoxy resin (in particular the DKL-based epoxy resin) to DGEBA reduces the initial decomposition temperature (IDT) likely due to the presence of low M_w lignin components in the bio-based epoxy resins.

3. The limiting oxygen index (LOI) of all lignin-based epoxy composites are higher than that of the conventional BPA-based epoxy resin indicating that the lignin-based epoxy composites are more effective fire retardants than the conventional BPA-based epoxy resin. Particularly, the highest value is obtained for 100% DKL-DDM system. 75% DKL-DDM, 100% DKL-DDM and 100% DOL-DDM can be classified as the self-extinguishing materials.

4. The DGEBA-DDM has a single decomposition step with $T_{max}$ at 426 ºC. The main volatile components identified are CO₂, CO, CH₄, H₂O, amine and carbonyl components and aromatic components. 100% DKL-DDM system has two decomposition steps. The first step occurs at 351 ºC where the main evolved gases are CO₂, H₂O and CH₄ and the second decomposition starts at 433 ºC. The 100% DOL-DDM system has a single decomposition-step at 413 ºC with the evolution of CO₂, CO, CH₄, H₂O, amine, carbonyl components and aromatic components as main gaseous components.
5. The wt.% amount of lignin-based epoxy resin in the bio-based epoxy composites had a significant effect on the activation energy at the beginning and final stages of the thermal decomposition process. With increasing the amount of the lignin-based epoxy resins in the composites, the activation energy reduces at the early stage of the process but drastically increases at the final stage of the decomposition. The degradation reaction can be explained as follows: initially, $\alpha < 0.3$, the weaker bonds such as ether linkages and side chains on benzene-propane can be broken, at $0.30 < \alpha < 0.75$ the main decomposition reactions may involve the cleavage of the C-C and $\beta$-$\beta$ bonds, finally, at $0.75 < \alpha < 0.95$, the predominant reactions can be related to the breakage of aromatic rings and 3-dimentional networks of lignin and epoxy resin.
7.5 References


Synthesis and Characterization of Hydrolysis Lignin-Based Epoxy Resins
Abstract

A novel bio-based epoxy resin was synthesized using de-polymerized hydrolysis lignin (DHL) as a feedstock under alkaline condition. The thermal and mechanical behavior of the resulting DHL-based epoxy resin were investigated using thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA), respectively. The chemical functionality of DHL-based epoxy resin was studied using Fourier Transformation Infrared spectroscopy (FTIR). The curing behavior of DHL-based epoxy resin with a selective curing agent (4,4’-diaminodiphenyl methane; DDM) was also investigated using differential scanning calorimetry (DSC). The curing process was found to proceed via a ring opening reaction involving the epoxy and the amine groups followed by etherification reactions at the end. The cured DHL-based epoxy-DDM system demonstrated good thermal and mechanical performances, suggesting its potential of utilizing hydrolysis lignin – a byproduct/waste stream from cellulosic ethanol processes for the production of value-added bio-based materials.
8.1 Introduction

Epoxy resins, currently produced dominantly from petroleum-based chemicals of bisphenol-A (BPA) and epichlorohydrin, have an indispensable role in electronics and composites industries [1,2]. The depletion of fossil fuel resources and the environmental issues of their products/derivatives have encouraged industry and academia to seek for renewable resources for the production of epoxy resins [3–5].

Recently, several researches have been reported on the synthesis of bio-based epoxy resins from various renewable resources such as gallic acid [6], tannins, vegetable oils [7] and lignins [8,9]. The synthesis of lignin-based epoxy resins derived from de-polymerized organosolv lignin and depolymerized kraft lignin was described in details in Chapters 5 and in our previous papers [10,11]. The current study was focused on the synthesis of a sustainable epoxy resin from hydrolysis lignin (HL). The hydrolytic lignin, extracted from the residues of the cellulosic ethanol production, is commonly known as “enzymatic hydrolysis lignin (EHL)” As enzymatic hydrolysis processes of biomass normally operates under relatively mild conditions, the most active functional groups such as phenolic hydroxyl and alcoholic hydroxyl can be preserved [12]. As a consequence, the resulting EHL is expected to be more reactive in comparison with lignosulfonate lignin or kraft lignin [12,13]. Enzymatic hydrolysis lignin is usually used as a fuel in combustion or gasification processes to generate steam or electricity [12]. In order to maximize its economic value, EHL could be used as a precursor for the production of bio-based chemicals such as phenol–formaldehyde resins, polyurethane foams, and epoxy resins. However, the crude hydrolysis lignin from a cellulosic ethanol process is not a pure lignin, but a complex mixture comprising 50-60% of lignin, 20-30% cellulose and hemicelluloses, and the rest is ash, and water.

Direct utilization of lignin as an alternative to bisphenol A (BPA) for the synthesis of bio-based epoxy resins would be challenging due to large molecular weight, less solubility in some solvents and the lower reactivity towards epichlorohydrin in the synthesis process. To address these challenges, commonly it is necessary to carry out some chemical modifications such as phenolation [14], hydroxyalkylation [15], methylolation [16] and de-polymerization [17] on lignin to enhance its reactivity in the reaction. Among these processes, de-polymerization of lignin has demonstrated its potential to provide a suitable feedstock for the synthesis of epoxy resins. It
enhances the activity of functional groups present on lignin with a substantial reduction in the average molecular weight of lignin.

In recent years, several studies have been reported on the production of lignin-based epoxy resins [18–20]. To the best of our knowledge, no published work has been conducted on the utilization of de-polymerized hydrolysis lignin as a feedstock in the synthesis of epoxy resins. So, the main objective of this research is the synthesis of a bio-based epoxy resin using a de-polymerized hydrolytic lignin. In the present study, hydrolysis lignin was de-polymerized in the presence of ethylene glycol (EG) at a relatively low pressure and reacted with epichlorohydrin to generate a lignin-based epoxy resin and the performance of the resin was evaluated. The curing kinetics of the bio-based epoxy resin was studied with a differential scanning calorimetry (DSC). In addition, the mechanical properties and the thermal performance of the lignin-based epoxy resin were investigated on a Universal testing machine (UTM) and a thermogravimetric analyzer (TGA), respectively.

### 8.2 Experimental

#### 8.2.1 Materials

Hydrolysis lignin (HL, hardwood) was supplied by FPInnovations. It was obtained as a byproduct from its proprietary hardwood fractionation process for bio-products such as sugars. The HL received is a yellowish powder with a very high average molecular weight (estimated > 20,000 g/mol), not soluble in water or any other common organic solvents. The HL contains >50-60 wt% lignin balanced by the residual cellulose and carbohydrates. A commercial epoxy resin (Araldite® GZ 540 X 90, DGEBA) was supplied by Huntsman with the epoxide equivalent weight (EEW) ≈ 295 g/eq and used as a reference to compare the curing kinetics and the thermo-mechanical properties of the lignin-based epoxy resin. All other chemicals, including ethylene glycol, acetone, sodium hydroxide, epichlorohydrin (ECH), tetrabutylammonium bromide (TBAB) and 4,4’-diaminodiphenyl methane (DDM) were purchased from Sigma-Aldrich and used without further purification. DDM was used as a curing agent for the lignin-based epoxy resin and the reference DGEBA. BGF fiberglass cloth (E-Glass, Plain weave fiber glass with 0.015 inches thickness) was purchased from Freeman, Ohio.
8.2.2 De-polymerization of Hydrolysis Lignin

De-polymerization of hydrolysis lignin (HL) was conducted in a 500 ml Parr stirred autoclave reactor at proprietary low-pressure process at 200°C for 1 h reaction in the presence of ethylene glycol (EG). Then, the reactor was quenched to room temperature by the cooling systems. The product was collected by washing the reactor with acetone. The collected product was filtered to remove the solid residue and removal the acetone using a rotary evaporator at 50°C. The filtrate was mixed with distilled water to remove ethylene glycol and other water soluble components. De-polymerized hydrolysis lignin (DHL) was collected by filtration of the mixture. Finally, DHL was dried at a vacuum oven at 60 °C for 6 h. The yield of de-polymerization process was ≈ 52%.

8.2.3 Synthesis of De-polymerized-Hydrolysis Lignin (DHL)-Based Epoxy Resin

In a typical run for the synthesis of DHL-based epoxy resin, 4 g of DHL was dissolved in 12 g epichlorohydrin (at an epichlorohydrin/lignin molar ratio of 6, the average molecular weight of monomers of lignin is 180 g/mol) to form a mixture of DHL/epichlorohydrin with additional of tetrabutylamunium bromide (TBAB, 2 wt.% of DHL) and 12 mL of distillated water charged into a 200 mL three-neck reactor. The reactor was heated up to 80 °C for 1 h under stirring. Then, the system was cooled to 55 °C and sodium hydroxide solution (NaOH/lignin molar ratio was 3) was added dropwise into the reactor for 15 min and maintained at the reaction temperature for 8h. Finally, the system was cooled down to the room temperature and the organic phase was separated. The non-reacted epichlorohydrin was removed using a rotary evaporator at 100 °C under a reduced pressure. The by-products were separated by dissolving the obtained product in acetone followed by filtration. Finally, acetone was removed using the rotary evaporator. The yield of DHL-based epoxy resin from the above epoxidation process was ≈ 95%.

8.2.4 Characterization

Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer) was used to analyze the chemical structure of the de-polymerized hydrolysis lignin (DHL), and the DHL-based epoxy resin by scanning from 500-4000 cm⁻¹. The total hydroxyl number/phenolic hydroxyl number of the DHL as well as the epoxy content (EC, weight percent epoxide) of DHL-based epoxy resin were measured according to ASTM D4247-11 and ASTM D1652-11 standard, respectively [21,22]. The Epoxy content was measured with a potentiometric titrator (Titroline 7000 Titrator). In this
method, the resins dissolved in 30 mL of methylene chloride (MECL) and 15 mL of tetraethylammonium bromide (TEAB) solution in acetic acid the resulting solution is titrated with perchloric acid solution. As the reaction progresses, the potential of the solution gradually increases until the reaction approaches to completion at which point the potential increases very quickly. This equivalence point of titration was used to calculate the epoxy content (EC) of resin as follows:

\[
EC = \frac{4.3 \times V \times N}{W}
\]  

(8-1)

Where V is the actual mL perchloric acid used to reach equivalence point, N is normality of perchloric acid reagent, W is the weight of the sample used and 4.3 is the theoretical molecular weight of the epoxide ring, 43, and it is adjusted to 4.3 for the calculation to percent epoxide.

The average molecular weight of DHL and DHL-based epoxy resins as well as the reference DGEBA epoxy resin were measured by using a GPC instrument (Waters Breeze 1525 binary lamp, UV detector set at 270 nm, Waters Styragel HR1 column at 40°C). The samples were dissolved in THF and the molecular weights were obtained using a method based on the molecular weight calibration curve as determined from the linear polystyrene standards.

The curing behavior of the lignin-based epoxy resin with amine was studied on a differential scanning calorimetry (Mettler Toledo DSC 1). A stoichiometric amount of the curing agent was mixed with the DHL-based epoxy resin and kept in a sealed vial at 5°C to prevent further reaction before the DSC analysis. For the DSC analysis, around 7 mg of the sample was loaded into an aluminum pan and the measurements were conducted from room temperature to 350°C at four different heating ramps 4, 6, 8 and 10 °C/min under a N₂ flow of 50 ml/min.

The thermal degradation of the thermally cured DHL-based epoxy resin was investigated by thermogravimetric analysis (TGA, Perkin Elmer Pyris1). The TGA measurements were conducted over 10-11 mg samples at a heating rate of 10 °C/min under nitrogen atmosphere from 50 °C to 800 °C.

Carver (hydraulic unit model 3925) hot press was used for the preparation of the fabricated fiber reinforces plastics (FRP). The pre-mixed DHL-based epoxy resin and conventional epoxy resin
(1/1 w/w) was blended with a stoichiometric amount of DDM as a curing agent and applied on the fiberglass mats (mass ratio of the epoxy matrix to the glass fiber is 1/1) using lay-up method. The prepared samples were cured using a curing procedure based on our DSC results in a hot press under 2000 psi. The cured composites were cut into dumbbell and rectangular shapes for tensile and flexural tests, respectively.

The tensile properties of the fiber-reinforced plastics were measured using a universal testing machine (UTM, Model Instron 8800 with a load cell of 250kN). The tensile tests were conducted according to ASTM D638-10 [23] at a crosshead speed of 5 mm/min and a gauge length of 50 mm. The flexural properties were determined using an Admet 7000 Universal Testing Machine on rectangular materials (127mm × 12.7mm × 3mm) according to ASTM D790-10 standard [24]. The flexural tests were performed on a three-point bending mode with a support span of 48 mm at a crosshead speed of 1.4 mm/min to the center of each specimen until failure.

8.2.5 Kinetic Study

The curing reaction of epoxy resin/amine system is a multi-step reaction and each step has its specific activation energy. Therefore, model-free isoconversional methods were used to evaluate the mechanism of the curing reaction to determine the dependency of activation energy of the curing reaction on the extent of curing (conversion, \( \alpha \), determined by the ratio of heat released up to a specific temperature to the total heat released from the entire curing process, calculated by integration of the DSC plots, as displayed in Figure 8-4). In the isoconversional principle, the reaction rate at a particular extent of conversion is a function of temperature [25]. During the curing of an epoxy resin, any changes in the activation energy can be associated with the curing mechanism and the dominate reaction can be predicted in a specific step of curing reaction [26]. Isoconversional models can be treated in two different methods, i.e., integral method and differential method. In the differential method, the common equation proposed by Friedman is expressed by Eq. (8-1) [27]:

\[
\ln(\beta \frac{d\alpha}{dt})_{\alpha,i} = \ln[A_{\alpha} f(\alpha)] - \frac{E_{\alpha}}{RT_{\alpha,i}} \quad (8-2)
\]

where \( \beta \) is the heating rate, the subscript \( i \) denotes the ordinal number of non-isothermal experiments conducted at different heating rates and the subscript \( \alpha \) denotes the extent of reaction.
In this method, $E_a$ is calculated from the slope of the plot $\ln(\beta \cdot d\alpha/dT)$ versus $1/T$ at a specific value of $\alpha$ for a set of 4 different $\beta$ (i.e., 4, 6, 8 and 10 °C/min), where it shall be noted that $T$ at a specific value of $\alpha$ was obtained from the $\alpha$ vs. $T$ plots.

8.3 Results and Discussion

8.3.1 Characteristics of Chemical Structure of DHL and DHL-Epoxy Resin

The chemical structure of de-polymerized hydrolysis lignin (DHL), the epoxidized DHL (DHL-Epoxy) and the fully cured DHL-Epoxy/DDM sample, compared with the reference DGEBA and the cured DGEBA/DDM, were analyzed using FTIR. All FTIR spectra are shown in Figure 8-1. The spectra of DHL and DHL-Epoxy resin are very similar except the vibration of the epoxy group in the spectra of DHL-epoxy resin at 915 cm$^{-1}$ which confirms the grafting of epoxy groups to DHL through the epoxidation reaction. The strong absorption band between 3200 and 3550 cm$^{-1}$ is associated with O-H stretching vibration of phenolic and aliphatic hydroxyl groups, and the absorbance at 1600 cm$^{-1}$ is related to the C=C aromatic bands.

After the curing of DHL-epoxy resin with DDM, the intensity of hydroxyl groups was reduced and the absorbance of the epoxide groups at 915 cm$^{-1}$ was completely disappeared. It means that all epoxy groups were consumed during the curing process and the hydroxyl groups reacted via the etherification reactions.
Figure 8-1 FTIR spectra of DHL, DHL-Epoxy resin and the cured DHL-Epoxy/DDM, compared with the reference DGEBA and cured DGEBA/DDM.

Average molecular weights, polydispersity index, hydroxyl number and Epoxy content of DHL and DHL-Epoxy resin, compared with the reference DGEBA and cured DGEBA/DDM, are presented in Figure 8-2 and Table 8-1. The weight-average molecular weight ($M_w$) and the polydispersity index (PDI) of DHL were found to be 2100 g/mol and 2.9, respectively. An increase in the average molecular weight ($M_w$) (from 2100 to 5530 g/mol) and PDI (from 2.9 to 4.6) was observed for the DHL-Epoxy resin, which implies the successful linking of several lignin molecules during the epoxidation reaction. The DHL has a total-OH number of 247 mgKOH/g and Phenolic-OH number of 130 mgKOH/g, and the epoxy content of DHL-epoxy resin was found to be around 5.13 as measured with the potentiometric titrator.
Figure 8-2 Molecular weight distribution of DHL and DHL-Epoxy resin.

Table 8-1 Average molecular weights, polydispersity index, hydroxyl number and Epoxy content of DHL and DHL-Epoxy resin, compared with the reference DGEBA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>PDI</th>
<th>Hydroxyl number (mgKOH/g)</th>
<th>Epoxy content $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total-OH</td>
<td>Phenolic-OH</td>
</tr>
<tr>
<td>DHL</td>
<td>710</td>
<td>2121</td>
<td>2.98</td>
<td>247</td>
<td>130</td>
</tr>
<tr>
<td>DHL-Epoxy</td>
<td>1183</td>
<td>5530</td>
<td>4.6</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>DGEBA</td>
<td>550</td>
<td>822</td>
<td>1.7</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ Weight percent epoxide

8.3.2 Curing Kinetics

DSC is an efficient technique to study the curing kinetics of thermosetting polymers. The lignin-based epoxy resin was blended with a stoichiometric amount of DDM and cured in DSC at various heating rates. Figure 8-3 displays the DSC thermographs of DHL-Epoxy/DDM and DGEBA/DDM systems at four heating rates. The obtained results are summarized in Table 8-2. The total heat of reaction was unchanged at all heating ramps for each sample indicating that the sample was completely cured at the specific heating rate and no vitrification occurred during the curing process. Also, a higher curing temperature was observed for the DHL-Epoxy-DDM sample in comparison to that of the conventional BPA-based epoxy sample (DGEBA/DDM) due to the high
viscosity of DHL-Epoxy resin that could retard the curing reaction. In addition, the total heat released for the lignin-based epoxy resin ($\Delta H \sim 100$ J/g) is lower than that for the BPA-based epoxy resin ($\Delta H \sim 290$ J/g), which can be caused by the lower epoxy content of DHL-Epoxy resin (Table 8-1).

![Figure 8-3 DSC profiles of DHL-epoxy/DDM (a) and DGEBA/DDM (b) at different heating rates.](image)
Table 8-2 DSC results from the thermographs of DHL-Epoxy/DDM and DGEBA/DDM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating Rate(°C/min)</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_p$ (°C)</th>
<th>$T_{\text{end}}$ (°C)</th>
<th>$\Delta H$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHL-Epoxy-DDM</td>
<td>10</td>
<td>79.6</td>
<td>121.7</td>
<td>244.7</td>
<td>104.6</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>68.3</td>
<td>114.8</td>
<td>236.6</td>
<td>97.4</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>64.6</td>
<td>107.6</td>
<td>231.6</td>
<td>109.8</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>56.6</td>
<td>102.1</td>
<td>216.3</td>
<td>96.7</td>
</tr>
<tr>
<td>DGEBA-DDM$^1$</td>
<td>10</td>
<td>76.8</td>
<td>160.2</td>
<td>260.4</td>
<td>290.0</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>67.7</td>
<td>153.7</td>
<td>249.7</td>
<td>288.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>61.5</td>
<td>146.0</td>
<td>231.1</td>
<td>279.9</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>51.6</td>
<td>135.7</td>
<td>215.3</td>
<td>288.7</td>
</tr>
</tbody>
</table>

$^1$DSC data from Chapter 6.

Figure 8-4 Fractional conversion ($\alpha$) as a function of temperatures while curing DHL-Epoxy-DDM at various heating rates.

The heat flow under the exothermic peaks was integrated and used to calculate the fractional conversion ($\alpha$) as well as the reaction rate ($d\alpha/dt$). Figure 8-4 displays a series of S-shaped curves which explores the extent of curing reaction in the entire process. The fractional conversion starts slowly at the beginning, increases exponentially at the middle and levels off at the final stage of
the curing process. It can be clearly observed that with increasing the heating rate, the degree of conversion shifts towards a higher temperature. The decrease in the reaction time of functional groups at a high heating rate may account for almost unchanged degree of conversion.

The fractional conversion ($\alpha$) and the rate of reaction of DHL-Epoxy-DDM were evaluated by an isoconversional method to determine the dependency of activation energy on the extent of the curing reaction. Before discussion about the distribution of activation energy, it is worth mentioning that activation energy represents the minimum required energy for starting a reaction. It means that reactions with a high value of activation energy have a lower reaction rate [28].

As illustrated in Figure 8-5, the activation energy of DHL-Epoxy-DDM sample remains approximately stable at the beginning of the curing process (< 25%) and then increases dramatically in the range of 25-70% conversion and finally goes up gradually after 75% degree of conversion ($\alpha = 0.75$), while the activation energy of DGEBA drops slowly with the incremental growth in conversion from 51 kJ/mol to 38 kJ/mol. The activation energy of DHL-epoxy-DDM system is higher than the value of DGEBA-DDM system during curing, which is caused by the low mobility of DHL-Epoxy resin due to its larger molecular weight and higher viscosity.

![Figure 8-5](image_url)  
**Figure 8-5** Dependence of activation energy on the extent of the curing reaction for the DHL-Epoxy-and the DGEBA-DDM system.
8.3.3 Thermal Performance

The thermal stability of the fully cured DHL-Epoxy/DDM and DGEBA/DDM was analyzed by TGA under nitrogen atmosphere. Figure 8-6 exhibits the TGA and DTG profiles of these cured epoxy resin systems. Table 8-3 presents the comparison between the thermal stability of the fully cured DHL-based epoxy/DDM and DGEBA/DDM system. The results reveal that DHL-based epoxy resin started to lose weight at a lower temperature than that of the conventional BPA-based epoxy resin and its maximum decomposition temperature is around 368 °C. This result suggests lower thermal stability of the lignin-based epoxy than the conversional BPA-based epoxy, which could be mainly due to the lower epoxy content (Table 8-1) and hence a lower cross-linking density of DHL-Epoxy resin. Besides, hydrolysis lignin consists of hemicellulose and cellulose; hence it would be possible that the synthesized DHL-Epoxy resin contains some hemicellulose. Usually, the thermal stability of hemicellulose is lower than that of the lignin [28,29]. Therefore, the decomposition of DHL-Epoxy resin at a relatively lower temperature (below 300°C) could also be due to the decomposition of hemicellulose present in it. On the other hand, however, the fixed carbon residue (CR) of DHL-Epoxy/DDM is 38% at 800 °C (corresponding to a limiting oxygen index (LOI) of 32.7, which makes DHL-Epoxy/DDM as a “self-extinguishing” material [30]), much higher than that of DGEBA-DDM (CR 12.5%, and LOI of 22.5).
Figure 8-6 TGA and DTG profile of DHL-Epoxy-DDM and DGEBA-DDM.

Table 8-3 Thermal decomposition of the fully cured DHL-Epoxy-DDM and DGEBA-DDM at 10ºC/min heating rate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_5$ (ºC)</th>
<th>$T_{max}$ (ºC)</th>
<th>$T_{50}$ (ºC)</th>
<th>CR (%)</th>
<th>LOI²</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHL-Epoxy-DDM</td>
<td>213</td>
<td>368</td>
<td>438</td>
<td>38</td>
<td>32.7</td>
</tr>
<tr>
<td>DGEBA-DDM</td>
<td>360</td>
<td>405</td>
<td>417</td>
<td>12.5</td>
<td>22.5</td>
</tr>
</tbody>
</table>

¹ Carbon residue at 800ºC
² Limiting oxygen index: $LOI = 17.5 + 0.4CR$

8.3.4 Mechanical Performance

The mechanical properties of the cured fiberglass reinforced DGEBA and 50% DHL-Epoxy plastics were measured by UTM machine. The tensile strength and the flexural fracture strength are recorded as the maximum applied stress prior to failure. The modulus of elasticity (or Young’s modulus) and flexural modulus were determined from the slope of respective stress-strain (or load-displacement) diagrams. The obtained results are given in Table 8-4. Clearly, the mechanical properties of the cured fiberglass reinforced DGEBA and 50% DHL-Epoxy plastics are actually closely comparable, suggesting good potential of application of the DHL-based epoxy resins as a
polymer matrix to substitute or partially substitute BPA-based epoxy for manufacture of bio-based fiber-reinforced plastics or composites.

**Table 8-4** Tensile and Flexural properties of the DDM cured fiberglass reinforced DGEBA and 50%DHL-Epoxy plastics.

<table>
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**8.4 Conclusions**

In this study, a bio-based epoxy resin was synthesized from de-polymerized hydrolysis lignin (DHL). The gross yield of the grafting process was approx. 95%. The chemical, physical, thermal and mechanical properties of the DHL-epoxy are characterized compared with a conventional BPA-epoxy resin (DGEBA). The FTIR results confirmed the attachment of epoxy rings on the lignin structure. The GPC results confirmed the increase of the weight-average molecular weight ($M_w$) of DHL from 2100 g/mol to 5530 g/mol after the epoxidation reaction. The curing mechanisms and kinetics of DHL-epoxy resin with DDM were elucidated by DSC measurements. The activation energy of DHL-epoxy-DDM system is higher than the value of DGEBA-DDM system during curing, which is caused by the low mobility of DHL-epoxy resin due to its larger molecular weight and higher viscosity. The fully cured DHL-epoxy-DDM was found to have higher carbon residue and limiting oxygen index (LOI) than that of the commercial BPA-based epoxy resin. The mechanical properties of the cured fiberglass reinforced DGEBA and 50%DHL-Epoxy plastics are actually closely comparable, suggesting good potential of application of the DHL-based epoxy resins as a polymer matrix to substitute or partially substitute BPA-based epoxy for manufacture of bio-based fiber-reinforced plastics or composites.
8.5 References


Conclusions and Future Work
This chapter summarizes the major findings and contributions from studies conducted in this research work. The recommendations for future works pertaining to the improvement of current research are also provided.

9.1 Conclusions

The main aim of this research was to develop a novel method to synthesize of lignin-based epoxy resins. Three types of de-polymerized lignins, namely kraft lignin, organosolv lignin and hydrolysis lignin, were used as raw materials for synthesis of bio-based epoxy resins under alkaline condition and in the presence of a phase transfer catalyst. The influence of the synthesis parameters including the reaction temperature, the reaction time, NaOH/lignin molar ratio and epichlorohydrin/lignin molar ratio were investigated and the optimum conditions for synthesis of the bio-based epoxy resins with high epoxy content and high yield of reaction were found. Then, the synthesized bio-based epoxy resins were cured with the common curing agents of epoxy resins, i.e. diaminodiphenyl methane (DDM), diethylenetriamine (DETA) to monitor the curing process and to evaluate their curing kinetics parameters. In addition, the lignin-based epoxy resins were mixed with the conventional BPA-based epoxy resin (DGEBA) at different percentages (0-100 wt.%) to produce lignin-based epoxy composites. The curing kinetics, the mechanical properties and the thermal stability of the prepared lignin-based epoxy composites were characterized.

The following detailed conclusions could be drawn from this research:

1. The molecular weight of the original lignin was reduced through a de-polymerization process, and a lignin-based epoxy resin was produced with suitable average molecular weight and distribution for applications. In this work, organosolv lignin was de-polymerized in the presence of hydrogen and then modified by epoxidation. The epoxidation process was conducted under various conditions to investigate the factors affecting product yields and properties. By increasing the molar ratio of epichlorohydrin/lignin, the product yield generally increased, and the molecular weight of the lignin-based epoxy resin generally decreased. However, the effects of other factors such as reaction time and reaction temperature on product yield and properties are complex.

2. For both original lignin and reductively de-polymerized lignin, the TGA measurement showed only one mass loss event in the range of 30°C–700°C, and the DSC analysis did
not show any exothermic peak in the same temperature range. In contrast, the prepared lignin-based epoxy resins showed two mass loss events in the TGA measurement: the first at around 200°C–300°C, and the second above 300°C, corresponding to homopolymerization (curing) of the lignin-based epoxy samples (as evidenced by the DSC measurement on the same sample) and thermal degradation of the lignin-based epoxy resins, respectively.

3. Epoxy resin was synthesized using de-polymerized organosolv lignin (DOL) in various conditions. The effects of the variable parameters including reaction time, reaction temperature and NaOH/DOL molar ratio on the reaction yield and epoxy content were investigated using central composite design. The obtained polynomial equations can be used to predict the yield and epoxy content of the products. The optimum conditions were predicted and validated by the experimental data. The optimum conditions determined are 8h at 55°C with 6.3 NaOH/DOL molar ratio, obtaining an epoxy resin with a high epoxy content of ~8 and 99% reaction yield.

4. The overall activation energy of all resin systems is 40-82 kJ/mol. The overall activation energies of both DOL and DKL-based epoxy resins cured with DETA are higher than those cured with DDM, suggesting that an aromatic amine has better activity than an aliphatic amine for curing of the lignin-based epoxy resins.

5. Almost in the whole curing conversion range, the activation energy of DKL-based epoxy resins is lower than DOL-based ones, likely attributed to the chemical structure of DKL containing more hydroxyl groups, which promote the curing process.

6. For the lignin-based epoxy resins cured with DDM, the activation energy increases with increasing the curing extent, while the activation energy of DKL-epoxy or DOL-epoxy cured with DETA generally decreases with increasing the curing conversion. This difference might be attributed to different curing mechanisms.

7. The DKL-based epoxy resins are more thermally stable than the DOL-based epoxy resins. The lignin-based epoxy samples cured with DDM curing agent have higher thermal stability than those cured with DETA. However, the thermal stability of all lignin-based samples is comparable to the thermal properties of the petroleum-based epoxy resins.

8. The char yields at 800 °C for all the lignin-based epoxy resins are in the range of 23-38 %, much higher than of the conventional BPA-based epoxy resins. The char yield of DKL-
DDM at 800 °C is as high as 38%, suggesting that the DKL-DDM could be a promising substitute for the petroleum-based epoxy resins.

9. The BPA-based epoxy resin has the highest value of the curing reaction heat (enthalpy) of around 288 J/g, followed by DOL-based epoxy composites (170-210 J/g) and the DKL-based epoxy composites (round 83J/g). This difference in the curing reaction enthalpy may be attributed to the different epoxy contents (EC) in the epoxy resins tested.

10. The addition of a lignin-based epoxy resin (in particular the DKL-epoxy) to the BPA-based epoxy decreases its onset, peak and end-set curing temperatures likely because the presence of hydroxyl groups on the lignin-based epoxy resins could promote the curing process.

11. Blending a lignin-based epoxy with the conventional BPA-based epoxy at a low blending ratio (25 wt%) could promote the curing process likely via the presence of free hydroxyl groups on the structure of lignin-based epoxy resins. However, further increasing the percentage of lignin-based epoxy in the epoxy composites to above 25 wt.%, do not decrease the overall activation energies as predicted but generally increase overall activation energies. This is probably due to the fact that the viscosity of an epoxy composite system increases with increasing the amount of lignin-based epoxy, which compromises the promoting effects of the hydroxyl groups and hence retards the curing process.

12. The wt.% amount of lignin-based epoxy resin in the epoxy composites had a significant effect on $T_g$: $T_g$ decreases with increasing the amount of lignin-based epoxy in the epoxy composites up to 50 wt.% and afterwards with further increasing the amount (>50 wt%) of lignin-epoxy in the composites, the $T_g$ increases. $T_g$ of an epoxy composite comprising the DKL-based epoxy resin was higher than that with the DOL-based epoxy resin, which might be attributed to the greater hydroxyl content in the DKL-epoxy than that in the DOL-epoxy resin.

13. The FRPs prepared with bio-based epoxy resins comprising up to 50-75 wt% of lignin-based epoxy resins as matrices have better or comparable tensile and flexural strengths compared with the FRP with 100% BPA-based epoxy resin. For modulus of elasticity and flexural modulus, the FRPs prepared with all bio-based epoxy resins comprising up to 100 wt% of lignin-based epoxy resins have better or comparable properties than the FRP with 100% BPA-based epoxy resin.
14. With increasing the percentages of DKL-epoxy (25-100 wt%) in the epoxy composites, the homogeneity of the epoxy composites decreases and the thermal decomposition peak gradually broadens and for the epoxy composites comprising 75% DKL-epoxy and 100% DKL-epoxy two distinct peaks were observed.

15. The addition a lignin-based epoxy resin (in particular the DKL-based epoxy resin) to DGEBA reduces the initial decomposition temperature (IDT) likely due to the presence of low $M_w$ lignin components in the bio-based epoxy resins.

16. The limiting oxygen index (LOI) of all lignin-based epoxy composites are higher than that of the conventional BPA-based epoxy resin indicating that the lignin-based epoxy composites are more effective fire retardants than the conventional BPA-based epoxy resin. Particularly, the highest value is obtained for 100% DKL-DDM system. 75% DKL-DDM, 100% DKL-DDM and 100% DOL-DDM can be classified as the self-extinguishing materials.

17. The DGEBA-DDM has a single decomposition step with $T_{\text{max}}$ at 426 °C. The main volatile components identified are CO$_2$, CO, CH$_4$, H$_2$O, amine and carbonyl components and aromatic components. 100% DKL-DDM system has two decomposition steps. The first step occurs at 351 °C where the main evolved gases are CO$_2$, H$_2$O and CH$_4$ and the second decomposition starts at 433 °C. The 100% DOL-DDM system has a single decomposition-step at 413 °C with the evolution of CO$_2$, CO, CH$_4$, H$_2$O, amine, carbonyl components and aromatic components as main gaseous components.

18. The wt.% amount of lignin-based epoxy resin in the bio-based epoxy composites had a significant effect on the activation energy at the beginning and final stages of the thermal decomposition process. With increasing the amount of the lignin-based epoxy resins in the composites, the activation energy reduces at the early stage of the process but drastically increases at the final stage of the decomposition. The degradation reaction can be explained as follows: initially, $\alpha < 0.3$, the weaker bonds such as ether linkages and side chains on benzene-propane can be broken, at $0.30 < \alpha < 0.75$ the main decomposition reactions may involve the cleavage of the C-C and $\beta$-$\beta$ bonds, finally, at $0.75 < \alpha < 0.95$, the predominant reactions can be related to the breakage of aromatic rings and 3-dimentional networks of lignin and epoxy resin.

19. A bio-based epoxy resin was synthesized from de-polymerized hydrolysis lignin (DHL).
The gross yield of the grafting process was approx. 95%. The GPC results confirmed the increase of the weight-average molecular weight ($M_w$) of DHL from 2100 g/mol to 5530 g/mol after the epoxidation reaction. The activation energy of DHL-epoxy-DDM system is higher than the value of DGEBA-DDM system during curing, which is caused by the low mobility of DHL-epoxy resin due to its larger molecular weight and higher viscosity.

20. The fully cured DHL-epoxy-DDM was found to have higher carbon residue and limiting oxygen index (LOI) than that of the commercial BPA-based epoxy resin.

21. The mechanical properties of the cured fiberglass reinforced DGEBA and 50% DHL-Epoxy plastics are actually closely comparable, suggesting good potential of application of the DHL-based epoxy resins as a polymer matrix to substitute or partially substitute BPA-based epoxy for manufacture of bio-based fiber-reinforced plastics or composites.

### 9.2 Future Work

1. The final properties of lignin-based epoxy resin depend on its average molecular weight. Therefore, it is needed to carry out more research on the de-polymerization process of lignin to develop a novel method of de-polymerization and optimize the process parameters in order to decrease the average molecular weight and generate a valuable bi-phenolic compounds to substitute bisphenol-A in the synthesis of epoxy resins.

2. Technoeconomical analysis of the whole process of synthesis of epoxy resin including the de-polymerization process and epoxidation process should be investigated before its commercialization.

3. Although the synthesized lignin-based epoxy resins exhibit acceptable thermal and mechanical properties, more research is needed to enhance its epoxy content via other epoxidation reactions.
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