Development of Bio-based Phenol Formaldehyde Novolac Resins Using Mountain Pine Beetle Infested Lodgepole Pine Barks

By

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A thesis submitted in conformity with the requirements of the degree of Master of Applied Science

Faculty of Chemical Engineering and Applied Chemistry

University of Toronto

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2014

Abstract

In this study, mountain pine beetle (MPB; Dendroctonus ponderosae) infested lodgepole pine (Pinus contorta) barks were converted to phenol substitutes using bark phenol liquefaction with sulfuric acid and hydrochloric acid catalysts. The bio-based phenol formaldehyde novolac resins were synthesized and characterized. The applications of these synthesized bio-based novolac PF resins in preparing thermal molding composites were also investigated.

It was found that both acid catalysts were effective in the bark-phenol liquefaction for obtaining the adequate phenol substitutes from MPB infested lodgepole pine bark. The synthesized bio-based novolac PF resins have higher molecular weight, more complex resin structures and comparable curing behavior and thermal stability to the reference novolac PF resins without liquefied bark components. The HCl acid-catalyzed liquefied bark novolac PF resins were successfully molded into composites with comparable mechanical properties, thermal stability, bonding performance, and enhanced water resistance in comparison to the lab-made control novolac PF resin.
Acknowledgements

First and foremost, I would like to take this opportunity to express my sincere gratitude to my supervisors, Prof. Ning Yan and Prof. Ramin Farnood, for their excellent mentorship and extraordinary support in this thesis process. With their invaluable help and insights, indispensable guidance and advice, generous support, constant patient, trust and encouragement, I was able to complete my thesis on time with satisfying outcomes. Their dedication and passion to work and commitment to excellence taught me more than just how to complete an excellent research work, but a dedicated working behavior. It was my honor and pleasure to have them as my supervisors. Thank you Prof. Yan and Prof. Farnood for giving me the great opportunity to work with you. This fulfilling study experience, as a master student, would definitely be one of the most valuable experiences in my life.

I would like to give my deepest appreciations to Yong Zhao, a postdoc in Prof. Yan’s research group, for his generous help and support, wise advices, guidance and encouragement during my master study. I would never forget those countless days and nights that we spent at the lab doing experiments. I would never forget how we solve problems and bottlenecks together for my experiments. I would also never forget the excitement when our first paper was published. Thank you very much for being my mentor and friend during my thesis study. Although my master study will be completed soon, our friendship will never end. Looking forward to work with you in the future.

I am notably indebted to my committee/examination member, Prof. Jia and Prof. Sain, for being very gracious and generous with their time.

I would like to express my most sincere thanks and love to my parents for their unconditionally love, encouragement and support throughout the duration of my study. Without them, I wouldn’t be who I am today and all the achievement and honor belong to them.
I would like to extend my utmost gratitude to all my beloved friends. Thank you all for your constant encouragement and support throughout my entire graduate study. I would like to express my special thanks to the following person here. Thank you Lanny for always being supportive, caring, understanding and overcoming all the frustrations with me during my master study. Thank you Elain for being my best friend, standing by my side all the time, sharing my tears and happiness and constantly giving me reasons to cheer. Thank you Davis for being by my side, pro-reading my writings, and always being inspiring, earnest, and patient. Words cannot express my thankfulness and I am feeling so blessed to have all of you in my life.

I would also like to convey thanks to my home department, the department of Chemical Engineering & Applied Chemistry, and the Faculty of Forestry at the University of Toronto for providing the funds and laboratory facilities in order to make this thesis possible.

Finally, I would like to thank all my colleagues in Prof. Yan and Prof. Farnood’s research group. Thank you all for your generous help and providing such nice working environment for my research study.
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List of Acronyms

CAGR    Compounded Annual Growth Rate
CNSL    Cashew nutshell liquid
DHB    2,5 – dihydroxy benzoic acid
DPM    Diphenylmethanes
DSC    Differential Scanning Calorimetry
FTIR    Fourier transfer infrared spectroscopy
GC-MS    Gas chromatography-mass spectrometry
HCl    Hydrochloric acid
HHDP    Hexahydroxydiphenic acid
HMTA    Hexamethylenetetramine
HPLC    High performance liquid chromatography
H₂SO₄    Sulfuric acid
Lab PF    Lab-made control novolac PF resins without bark components
LB-S    Sulfuric acid-catalyzed liquefied bark
LB-C    Hydrochloric acid-catalyzed liquefied bark
LBPF    Liquefied bark phenol formaldehyde
LBPF-S    Liquefied bark novolac PF resin with sulfuric acid-catalyzed liquefied bark components
LBPF-C    Liquefied bark novolac PF resin with hydrochloric acid-catalyzed liquefied bark components
LWPF    Liquefied wood phenol formaldehyde
Mn    Number average molecular weight
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>MOE</td>
<td>Young’s modulus</td>
</tr>
<tr>
<td>MPB</td>
<td>Mountain pine beetle</td>
</tr>
<tr>
<td>Mw</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>N/A</td>
<td>Not applicable</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>OSB</td>
<td>Oriented strand board</td>
</tr>
<tr>
<td>PF</td>
<td>Phenol-formaldehyde</td>
</tr>
<tr>
<td>PPF</td>
<td>High-ortho novolac resins</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analyzer</td>
</tr>
<tr>
<td>TS</td>
<td>Thickness swelling</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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Chapter 1

Introduction

1.1 Motivation and Significance

Phenol formaldehyde (PF) novolac resins are produced from the addition and condensation reactions between phenol and formaldehyde under acidic condition with formaldehyde to phenol ratio of less than one. Novolac resin is a linear thermoplastic polymer with partially cross-linked structure; thus, a subsequent step, which involves the addition of hexamethylenetetramine (HMTA) as curing agent, is required in order to achieve a fully cross-linked structure. Phenol formaldehyde novolac resins have been extensively used as molding compounds, wood adhesives, frictional materials in transportation sector, adhesives, coatings and thermal insulation materials due to their outstanding mechanical properties, bonding performance, water and heat resistance and durability [1]. According to a marketing research conducted by the Axis Research Mind on a global market watch of phenol formaldehyde resins [2], the global volume market value for phenol formaldehyde market in 2016 is projected to increase to 16 million tons. Based on the geographical analysis for applications of phenol-formaldehyde resins during the analysis period of 2011-2016, the highest Compounded Annual Growth Rate (CAGR) is predicted in the Asia-Pacific market at 15.2% following by the Europe with a growth rate of 14.3%. The American market is foreseen to have a CAGR of 12.2%. Therefore, PF resins have a bright future with high market demands and large commercial market values.

Phenol, as a raw material of the current phenol formaldehyde resin production, is primarily derived from fossil fuel resources, such as petroleum and coal; therefore, the production and price of phenol relies on the availability of fossil fuels. The increasing demand and the extensive consumption of fossil fuels in both developed and developing countries have caused various concerns on the depletion of fossil reserves in recent years. Despite the energy shortage, the environmental concerns, such as climate change and negative environmental impacts, associated with use of petroleum-based material also
drew the public attentions. Thus, there is a strong interest in searching environmental friendly and renewable resources as alternative feedstock to replace the petroleum-based phenol in phenolic resin production. [3]

Biomass is a renewable organic resource that can be utilized as an alternative to replace fossil fuels for the sustainable production of various petroleum-based chemicals. Barks, a renewable non-food based biomass material, are largely available as waste residues from forest mill sites. These large amounts of bark residues are currently treated as waste or burned with other woody residues to generate heat for the forest mill sites. However, barks have relatively low heating value especially for wet barks. Therefore, there is a great demand for the developments of suitable and efficient commercial process for converting bark residues into valuable products. In general, bark has similar cellulose and hemicelluloses content as wood in the fiber portion. However, bark contains more minerals, extractives and phenolic compounds than wood. The phenolic compounds (Figure 1.1), such as lignin and tannin, contain reactive phenolic moieties that can react towards to formaldehyde. Therefore, barks become the potential partial substitute of petroleum-based phenol in various types of bio-based PF resin synthesis due to its high phenolic content. [4 – 5]

![Phenolic compounds from bark](image)

**Figure 1.1** Phenolic compounds from bark. [4]
In the recent decades, severe mountain pine beetle (MPB; *Dendroctonus ponderosae*) infestation outbreaks in forests of western Canada. As the most serious mountain pine beetle epidemic in the North American history, the mountain pine beetle affected overall 18.1 million hectares forested lands in British Columbia since 2000 [6]. Mountain pine beetles live on the lodgepole pine (*Pinus contorta*) trees; however, they can be carried by the wind currents and travel from British Columbia to the northwestern and north-central part of Alberta [7]. Infested trees were harvested in order to slow the spread of the MPB and reduce the further attack, which produces large amount of available MPB infested lodgepole pine biomass for use [8]. In order to incorporate mountain pine beetle infested lodgepole pine bark, as a raw material, into PF resin formulation; it is necessary to effectively convert bark components to partial phenol substitute. Studies have found that acid-catalyzed phenol liquefaction can effectively convert biomass materials into phenol substitute, which can be utilized to synthesize bio-based phenolic resin for thermal-molding and wood adhesive applications [3, 9 – 10]. The phenol liquefied biomass materials have very similar molecular structures (Figure 1.2) as novolac resin, which could be used directly as novolac resins or could be further reacted with formaldehyde to form thermoplastic resins under acidic condition [11 – 13]. However, the chemical compositions of bark varies as a function of species, history of disturbance, environmental condition as well as the position of which the bark sample was taken due to its complex heterogeneous structure. The variable chemical structure and reactivity of the bark phenolic compounds increases the difficulty to incorporate bark component into the commercial PF resin formulation. [4 – 5, 9 – 10, 14 – 16]

![Figure 1.2 Typical phenol liquefied biomass materials [11 – 13].](image-url)
Previously, Y. Zhao et al. [17 – 18] have successfully synthesized PF resol resins using the liquefied MPB infested lodgepole pine bark under alkaline conditions. Studies have found that the synthesized PF resol resins with liquefied MPB infested lodgepole pine bark component demonstrated comparable dry and wet bonding strength to a commercial oriented strand board (OSB) face layer PF resol resin. However, no previous studies have been reported on incorporating liquefied MPB infested lodgepole pine barks in the novolac PF resin synthesis. Limited researches have investigated the effects of the resin formulation on the curing behavior and thermal stability of the synthesized bio-based PF novolac resins and the application of these bio-based PF novolac resins in thermal molding. Hence, it would be highly beneficial to the forest industry if these MPB infested lodgepole pine barks could also be converted into alternative substitutes for petroleum based phenol and partially replace phenol in the novolac PF resin production.

1.2 Scope

In this thesis study, the mountain pine beetle infested lodgepole pine bark was liquefied in phenol using either sulfuric acid or hydrochloric acid as the catalyst. The liquefied bark components were directly used as phenol substitute to partially replace petroleum-based phenol in the bio-based PF novolac resin synthesis. The scope of this thesis study includes following aspects:

1. To investigate the effect of catalyst types on the acid-catalyzed bark phenol liquefaction process and the properties of the resulting liquefied bark products.
2. To study the influence of acid-catalyzed liquefied bark components on the physical properties, curing behaviors, resin structure, and thermal stability of the resulting bio-based novolac PF resin
3. To examine the mechanical properties, water resistance, thermal stability, and the bonding performance of the molding composites prepared using the bio-based novolac PF resins as matrix material.
4. To relate the resin properties of the bio-based novolac PF resin to the characteristics of the resulting molding composites.
1.3 Hypotheses

The hypotheses for this thesis study were stated as following:

1. Acid-catalyzed phenol liquefied bark components can be incorporated into novolac PF resin formulation as phenol substitute to partially replace petroleum-based phenol.

2. Sulfuric acid and hydrochloric acid will have different effects on the bark phenol liquefaction. The resulting liquefied bark components, liquefied bark novolac PF resins and the molding composites prepared from different acid-catalyzed liquefied bark novolac PF resins will have different properties, characteristics and performance.

3. The bio-based novolac PF resin with acid-catalyzed phenol liquefied bark components will have comparable resin properties and performance to the lab-made control novolac PF resin, which does not contain any bark components.

4. Acid-catalyzed phenol liquefied bark components will not jeopardize the bonding performance of the resulting bio-based novolac PF resin and will be compatible with reinforcement fibers and other additives in molding the composites.

5. The synthesized bio-based novolac PF resin with acid-catalyzed phenol liquefied bark components can be used as matrix to make molding composites, which will have comparable mechanical properties, water resistance and thermal stability as the reference molding composite made from lab-made control novolac PF resin.

1.4 Objectives

The overall objectives of this study are to liquefy the mountain pine beetle infested lodgepole pine bark using phenol and different types of acid catalysts and then use the liquefied bark components as a partial substitute of petroleum-based phenol in the phenol formaldehyde novolac resin formulation, to formulate a bio-based liquefied bark novolac PF resins. To investigate the impact of different types of acid-catalyzed phenol liquefied bark components on the structure, composition, resin properties, curing behavior and thermal stability of the bio-based novolac PF resins. To prepare the molding composites
using the bio-based PF novolac resins and to investigate the mechanical properties, water resistance, bonding performance and thermal stability of the resulting molding composites and relate the composite’s performance to the resin properties. The specific objectives for each stage of the study was identified as following:

1. To liquefy mountain pine beetle infested lodgepole pine bark using phenol and either sulfuric acid or hydrochloric acid catalyst in order to obtain adequate phenol substitutes.
   - To study the effects of different catalysts on liquefaction yield of acid-catalyzed bark phenol liquefaction, unliquefied bark residues content, and the amount of free phenol remained in the liquefied bark fraction.
   - To investigate the properties and characteristic of resulting acid-catalyzed liquefied bark products using different types of acid catalysts.
   - To evaluate the compositions of the corresponding residues from bark liquefaction with different types of acid catalysis.

2. To synthesize the bio-based acid-catalyzed liquefied bark PF novolac resins.
   - To incorporate phenolated bark components from the phenol bark liquefaction using different acid catalysts into the liquefied bark PF novolac resin formulation.
   - To synthesize the liquefied bark PF novolac resin and test the resin performance.

3. To investigate and characterize the bio-based acid-catalyzed liquefied bark PF novolac resins.
   - To investigate the resin properties of the bio-based liquefied bark novolac PF resins.
   - To study the dynamic and isothermal curing behavior of the liquefied bark novolac PF resins.
   - To evaluate the impact of different acid-catalyzed liquefied bark components on the structure and composition of the resulting bio-based liquefied bark novolac PF resin.
• To investigate the effects of different acid-catalyzed liquefied bark components on the thermal stability and thermal degradation kinetics of the bio-based novolac PF resins.

4. To prepare and characterize the molding composites prepared from different liquefied bark novolac PF resins.
   • To study the mechanical properties of the molding composite prepared from different liquefied bark novolac PF resins.
   • To test the water resistance of the molding composite prepared using different liquefied bark novolac PF resins.
   • To evaluate the impact of different acid-catalyzed liquefied bark components on the thermal stability of the resulting molding composites.
   • To investigate the bonding performance between the different liquefied bark PF novolac resins and the reinforcement fiber particles.
   • To study the mechanical properties, water resistance, thermal stability, and bonding performance of the resulting composites in relation to the resin properties.

1.5 Thesis overview

This thesis contains seven chapters. Chapter 1 introduces the motivation and significance, scope, hypothesis and objectives of this study. Chapter 2 includes a general review on the background of current phenol formaldehyde resins synthesis and its commercial applications, and a detailed review on previous research studies and literature findings on bio-based novolac PF resins preparing from renewable bio-based phenol and its adhesive application. Chapter 3 provides the detailed experimental approaches on materials, experimental techniques, equipment, and methods used in the study, including the acid-catalyzed bark phenol liquefaction methods, the bio-based liquefied bark PF novolac resin synthesis, preparation procedures of the molding composites using the synthesized bio-based liquefied bark novolac PF resins, and the characterization techniques for testing both bio-based liquefied bark novolac resins and the corresponding molding composites.

Chapter 4 discusses the characterization results of the liquefied bark products obtained
from the bark phenol liquefaction using different types of acid catalyst. Chapter 5 discusses the characterization results, resin properties, curing behavior and thermal stability of the bio-based liquefied bark novolac PF resins. Chapter 6 explores the application of the synthesized bio-based liquefied bark novolac PF resins in preparing the molding composite and discusses the performance of the resulting molding composites. Chapter 7 gives the summary of all the major findings from this thesis and concludes the thesis with recommendations for future studies. The thesis overview is summarized in Figure 1.3 below.

Figure 1.3 Thesis overview
Chapter 2

Literature Review

2.1 Wood Adhesive

Wood adhesives are polymeric materials that can be physically or chemically interacted with the wood surface to tightly bond pieces of wood together. Wood adhesives have a wide range of applications in our daily life including manufacture civil infrastructure, such as plywood and laminated building materials, as well as nonstructural applications such as furniture and floor coverings. Wood adhesives can be produced from either natural or synthetic sources. Synthetic adhesives are generally classified as thermoplastic or thermosetting resins due to the polymer’s nature after the curing process.

Thermoplastic polymers are soften and moldable upon heating with the ability to return to a solid state under room temperature through the cooling process. Vinyl is one of the major types of thermoplastic resin, which is commonly used in packaging. Thermosetting resins are usually in the liquid state under room temperature and form non-moldable cross-linked polymers during cure. Once the thermoset polymer has cured, it cannot be reshaped upon heating. However, thermosetting resins’ highly cross-linked nature provide them with several desirable mechanical and chemical properties such as strength, high modulus, durability, and chemical and thermal resistances, which favors thermosets in many industrial application. Amino resins, isocyanate resins, epoxy and phenolic resins are typical thermosetting resins used in industry. Among these four thermosetting resins, phenolic (PF) resins play a dominant role in industrial application such as molding, coating as well as use as the major adhesive for wood bonding. Moreover, PF resins are extensively utilized as engineering and commercial materials in commodity construction and transportation sector [19 – 21].

2.2 Phenol-Formaldehyde (PF) Resin

Phenol formaldehyde (PF) resins are a large group of oligomers and polymers, which consist of various structures as resulting products from the reaction of phenol and
formaldehyde. When the phenolic resins first introduced in the 1900s, they were primarily used in molding parts, insulating varnishes, industrial sheeting and coating. Later, phenolic resins were utilized as wood adhesives in wood and fiber bonding to make composite. Despite the innovations of new type of thermosetting resins and other high-performance polymeric materials, phenolic resin still retains its important application in these areas and further extended to high-technological development especially in electronics and aerospace. This is due to the highly stable nature of phenolic resins with ultimate mechanical strength acquired during the curing process. Besides, they are inherently resisted against heat, flame and chemicals, which brings the application of PF resins to aerospace and transportation industry as thermo-structural materials [20–21]. Phenolic resins are synthesized from the petroleum-based phenol or substituted phenol with formaldehyde under either alkaline or acidic condition, which are known as resol and novolac PF resins accordingly [19].

2.2.1 Resol Resins

Resol resins are produced under alkaline condition with base catalyst and formaldehyde to phenol ratio of greater than one. During the resin synthesis, phenol is first reacted with formaldehyde, in the form of formaldehyde monohydrate (a.k.a. methylene glycol), to form the hydroxymethyl-substituted phenol called methylol phenol (Figure 2.1) [22].

![Figure 2.1](image)

**Figure 2.1.** The reaction of phenol with formaldehyde to form methylol phenol [22].

Due to the highly reactive methylol phenol, there are three different types of formaldehyde-derived moieties formed on the molecule of resol resin, which are methylene bridges (Figure 2.2), dimethylene ether bridges (Figure 2.3), and hydroxymethyl groups (Figure 2.4). Two methylol phenol molecules can react with each other to form a longer chain hydroxymethyl-substituted phenol unit with methylene bridge linkage (Figure 2.2). Methylol phenol can also react with itself to form
dimethylene ether bridge on each resol molecule (Figure 2.3). The dimethylene ether bridge is more favorable and stable in the ortho-position than in the para-position. As shown in Figure 2.5, without further addition of catalyst, dimethylene ether bridge can be converted into methylene bridges upon heating by eliminating formaldehyde. The resultant formaldehyde can further react with phenol under alkaline condition to form methylol phenol. Moreover, methylol phenol reacts with phenol to cause the direct condensation of hydroxymethyl group with the formation of the methylene bridge in resol resin molecule (Figure 2.5) [22-23].

Figure 2.2. The reaction of two methylol phenols form a longer chain hydroxymethyl-substituted phenol unit linked by methylene bridges [22].

Figure 2.3. Methylol phenol can react with itself to form dimethylene ether bridge on each resol molecule [22].

Figure 2.4. The direct condensation of hydroxymethyl group as a result of methylol phenol reacts with phenol to form the methylene bridge in resol resin molecule [22].

Figure 2.5. Dimethylene ether bridge can be converted into methylene bridges by eliminating formaldehyde [22].
The use of excessive formaldehyde in the reaction ensures a sufficient number of active hydroxymethyl and dimethyl groups to achieve the polymerization during resin curing. Due to the presence of active hydroxymethyl groups, resol resins can be self-cured and cross-linked upon heating without addition of curing agent. Thus, the resol resins are usually referred as one-stage resins. However, the resol resins are unstable and sensitive to heat and acid because the use of excess formaldehyde in the reaction causes the condensations of hydroxymethyl groups to occur [19]. The polymerization of resol resins continues to happen at ambient temperature at a slow rate, which limited the shelf life of the resin. In general, these resins have a highly branched structure with the typical number average molecular weight (Mn) lies between 200 and 450 [22]. However, the resin structure and property are highly dependent on the concentration of raw materials, phenol to formaldehyde ratio, pH, catalyst type and its concentration, reaction temperature and time [23]. The main application of resol resins is used as wood adhesive for bonding wood panels, chipboards or fiber for constructional use. They are also commonly used for laminate manufacture and foamed plastics production [23].

2.2.2 Novolac Resins

The novolac resins are produced under acidic condition with formaldehyde to phenol ratio of less than one. The first step in the novolac resin synthesis is conversion of formaldehyde (methylen glycol) into the hydrated carbonium ion under the effect of acid catalyst (Figure 2.6). The hydrated carbonyl compound then attacks the phenol molecule on its para- and/or ortho- position to form the corresponding para- or ortho- benzylic ions with hydroxymethyl groups through dehydration reaction (Figure 2.6) [21]. Since hydroxymethly groups on the benzylic ions are unstable in acidic condition, these hydrated benzylic ions further react with additional phenol and add to the free para- and ortho- sites on the phenol molecule by creating a methylene bridge between two phenolic aromatic rings [21]. The resulting methylene linked ortho-ortho, ortho-para, and para-para bisphenols are shown in Figure 2.7. The para- site is twice more active than the ortho- site; however, each phenol molecule has two ortho- sites and only one para- site. Therefore, the fractions of ortho-ortho, ortho-para and para-para bridge are roughly even
in the reaction product. The ortho-para bridge is dominant, approximately 50-75%, in the acid-catalyzed novolac resins [21].

**Figure 2.6.** The reaction of formaldehyde and phenol in novolac resin [21].

Since reactions can happen at any of the three positions on each phenolic aromatic ring, the resulting novolac polymer acquires a complex structure with different polymer sizes and molecular weight up to 5000. The reaction terminates as all the formaldehyde are consumed leaving with approximately 10% of excess phenol, which can be remove along with water during the further distillation of the resin [22]. The reaction rate is directly related to the concentration of phenol, formaldehyde and the catalyst loading, while inversely proportional to the concentration of water. The rate of formation of methylene-linked bisphenols is 5-10 times higher than the rate of formation of benzylic ion intermediates [21]. At typical molecular weights of 500-1000, the novolac resins do not
have reactive hydroxymethyl groups because of the present of excess phenol in the reaction mixture. Therefore, novolac resins are relatively stable in comparison to resol resins and acquired a linear structure at relatively low molecular weight. At higher molecular weights of above 1000, branching occurs as the reactions continue between the end groups and unreacted phenol. End groups are more reactive than the backbone groups during the curing process. Therefore, branched resins with more end groups have faster curing time than resin with linear structure. Moreover, the resin structures and properties also depend on the catalyst type and reaction condition. The typical acid catalysts used in novolac resin synthesis are sulfuric acid, sulfonic acid, oxalic acid, phosphoric acid and hydrochloric acid [21].

2.2.2.1 Curing of Novolac Resins

Novolac resins are commonly referred as “two-stage” resins due to the fact that these resins are thermoplastic with partially cross-linked structure and a subsequent step is required in order to achieve fully cross-linked. This subsequent step involves the addition of a second reactive compound as curing agent, usually hexamethylenetetramine (HMTA), to harden the novolac resins [22]. Typically, 5-15% of HMTA are used to react with the resin and phenol in order to “thermoset” the resin by further linking and polymerizing the resin with methylene bridges between molecules.

![Figure 2.8. Curing reaction of novolac resin with HMTA [21].](image-url)
As shown in the Figure 2.8, benzoxazine is formed at the beginning of the curing reaction. Then all the benzoxazines are decomposed to benzylation intermediates before forming the final product diphenylmethanes (DPM). The large amount of ortho-ortho diphenylmethane end groups in the resin increase the resin’s reactivity towards HMTA. These diphenylmethane end groups react with HMTA to form benzoxazine first, and then decompose to form methylene bridges with the vacant sites on novolac molecules to increase the cross-linking density of the resin. \[21\] As a result, the cured resins have a complex three-dimensional polymer structure with high molecular weight, which enhance the resin’s hardness and resistant against heat and chemicals \[22\].

2.2.2.2 Applications of Novolac Resins

Novolac PF resins have a wide range of industrial applications in molding, manufacturing fiction materials for transportation sector, fabricating and bonding phenolic fiber, and using as reinforcement resin for rubber.

**Molding** - Novolac resins play an important role in the thermal molding industry. The mixture of novolac resins, curing agent (typically HMTA), reinforcement fillers and other additives, such as pigments, accelerating agent and lubricating agent, are treated to produce the moldable thermoset materials. In some nitrogen-sensitive electrical applications, in which the NH$_3$ generated from the reaction involving HMTA may corrode certain metals such as copper and silver, resol resins can be used as an alternative curing agent during the molding process. The novolac-based thermosetting molding materials have desirable flow characteristics and fast curing time. The molded products exhibit an outstanding resistance against heat, flame and chemical with desired hardness. Three typical processes for the novolac resin molding are compression, transfer and injection molding. Since the molding material becomes fluid upon heating, compression molding is the most suitable process for molding novolac resin with a typical temperature range between 140-190 °C and pressures from 13.8 to 55.5 MPa \[21\].

**Fiction materials** – The phenolic resin thermosets are molded to make phenolic friction materials, which are extensively used in transportation sector for brake linings, clutch
facings, and transmission bands. These friction materials have high temperature-independent coefficient of friction, high strength, durable against wear and abrasion, and resistant to moisture and hydraulic fluids. The mixtures of novolac resin and HMTA are also used as binders in friction linings. Modified novolac resins, by adding alkylated phenol, oil or cashew nutshell liquid (CNSL), with reduced hardness and increased abrasion resistance are used in brake linings [21, 23].

**Fibers and fiber bonding** – The novoloid fiber is the major type of phenolic fiber, which has at least 85% of cross-linked novolac resins content in the fiber composition. The uncured fibers are prepared from novolac resin with high molecular weight through the melt-spinning process. These fibers are then cured in formaldehyde solution with an acid catalyst. During the curing process, a fully cross-linked amorphous network is achieved through the formation of methylene and dibenzyl ether bridges. The cross-linked novoloid fibers are insoluble and infusible with low cross-linking density. The novoloid fibers are widely used as flame barriers in flame- and chemical-proof protective gears and furniture. Novoloid fibers can be used as an alternative to the asbestos in gasketing, packings, brake linings, and clutch facings. Novoloid fibers and papers are also used as flame-resistant coatings for wire and cable in electrical applications. Moreover, novolac-based resins can be used along with HMTA to bond organic fibers and produce bonded mats with high bonding and tensile strengths and good stability [21].

**Reinforcing resin for rubber** - The HMTA-cured novolac resins can be used as the reinforcing resin for increasing the hardness of rubber. The strong intermolecular bonds between the cross-linked phenol novolac and the vulcanized rubber cause the reinforcing effect to enhance the toughness of the rubber and allow it to grind hard molded pieces [23].

**Other applications** - Apart from above applications, the phenolic novolac resins are also used profoundly as binder and coating materials for sand in the production of shell molds and cores in the foundry industry. It is also effectively used as curing agents for epoxies in order to improve the epoxy resin’s functionality and cross-link density [21].
Furthermore, the novolac resins without cross-linking structure are soluble and highly compatible with other chemicals, which find use in various industries include vanishes, printing technology, epoxy resin manufacture, production of copying paper, tackifiers for rubber and crude oil separators. However, the applications of non-cross-linked novolac are less important than the cross-linked novolac resins [23].

2.3 Current Concerns

Natural resins were once predominated in the industry before the first synthetic resins were introduced in the early twentieth century through the polycondensation reaction of phenol and aldehydes. Synthetic resins replaced natural resins since the mid-twentieth century and extensively applied in industry [23]. However, synthetic resins are produced from petroleum-based chemicals. Phenol, as the raw material for phenolic resin production, is primarily derived from petroleum; therefore, the production and price of phenol relies on the availability of fossil fuels. The increasing demand and the extensive consumption of fossil fuels in both developed and developing countries have caused various concerns on the depletion of fossil reserves in recent years. This leads to the dramatic increase in the petroleum price, which directly affect the price and production of phenolic resins.

Despite the energy shortage, the environmental concerns associated with use of petroleum-based material also drew public attentions. First of all, burning of fossil fuels generate massive amount of carbon dioxide (CO\textsubscript{2}), which is the major part of greenhouse gases. The release of carbon dioxide into the atmosphere increases the greenhouse effect, which results in the global warming and climate change. Secondly, the sulphur dioxide (SO\textsubscript{2}) and nitrogen oxides (NO\textsubscript{x}) produced by burning fossil fuels are the main contributor to acid rain, which is directly associated with permanent damage to the environment such as destroy forests and acidify fresh water resources. Moreover, phenolic resins are not naturally degradable due to the highly cross-linked structure; therefore, the disposal of phenolic resin causes another environmental issue associated with the use of petroleum-based phenol. All these concerns, including energy shortage and negative environmental impacts, in regard to the use of petrochemical products drive
our interests in finding alternative, environmental friendly, sustainable, and renewable resources to replace the petroleum-based raw materials in phenolic resin production [3]. Biomass is a renewable organic resource that can be utilized as an alternative to replace fossil fuels for the sustainable production of biofuels and chemicals, which are primarily produced from fossil fuels. Biomass is mainly derived from the waste of agricultural and wood industry. With an annual production of approximately $20 \times 10^{10}$ tones, biomass becomes one of the most plenteous renewable sources of energy on earth. Biomass has much shorter growing cycle over fossil fuels, which promises the sustainable production and use of biomass [3, 24]. Besides the unlimited supplies of biomass, the associated environmental and economic benefits also encourage a greater use of biomass in petrochemical industries and energy sector. First of all, biomass is carbon neutral since the consumption of biomass or biomass-based products do not increase the net CO$_2$ emission to the atmosphere [3]. This recognition emerges from the fact that carbon dioxide released from consuming biomass products balanced by the carbon dioxide captured in the recent growth of biomass through the photosynthesis process. Therefore, using biomass fuels instead of fossil fuels would significantly lower the greenhouse gas level in the atmosphere and reduce the greenhouse effect. Secondly, biomass contains little amount of nitrogen and sulphur, hence, it does not contribute the SO$_2$ and NO$_x$ pollutants, which can cause acid rain, to the atmosphere [24]. Moreover, biomass is much less expensive compared to fossil fuels, such as petroleum and natural gas. Therefore, using biomass instead of fossil fuels in the production of fuels and chemicals would be more environmentally friendly and cost-effective.

There are generally four categories of biomass applying in energy generation nowadays, which are wood and agricultural products, solid waste, landfill gas and biogas, and alcohol fuels. Among these biomass sources, wood and agricultural products, including wood chips, bark, sawdust, corn, starch, and other agricultural residues, account for the major part in the industrial application of biomass [24]. Biomass feedstock used in petroleum and petrochemical industry is usually referred to lignocellulosic biomass. Lignocellulosic biomass is composed of typically 40-45% cellulose ([C$_6$(H$_2$O)$_4$]$_n$), 25-35% hemicellulose ([C$_5$(H$_2$O)$_4$]$_n$), 15-30% lignin ([C$_{10}$H$_{12}$O$_3$]$_n$) and the rest 10% are
made up by pectin, protein, extractives and ash [24]. Lignin is an aromatic phenyl-propane polymer linked by C-C or ether bonds retained a highly cross-linked, three-dimensional structure. Lignin is commonly used in pulping process to be dissolved by phenol for paper production. This indicated that lignin has a similar structure to phenol. Therefore, lignocellulosic biomass is expected to be a potential source of material to replace or partially replace phenol, the most expensive and petroleum based raw material, in the phenolic resin production [24].

2.4 Bark

Bark is generally referred to the outermost part of the tree stems and branches. Anatomically, bark is defined as all the plant tissues located at the outside of the vascular cambium including both live and dead cells generated by two cambia. Bark is a highly complicated and heterogeneous material comprised of two main tissue types, which are the phloem and the periderm. The phloem is the main component of the inner bark layer, which is formed adjacent to the vascular cambium. The phloem tissues consist of important sieve elements that are responsible for transporting nutrients, carbohydrates and water between leaves and roots. The inner layer of the tree bark is relatively thin and active with light color. The periderm is formed by the cork cambium and usually known as the outer bark layer. The outer bark is relatively complex and physiologically inert, which is used to protect the vascular cambium and prevent water and nutrients loss. Large amount of surplus bark residues are produced from forest mill sites, which become the most intractable problem that the wood industry is facing nowadays. These largely available bark residues are currently treated as waste or burned with other woody residues to generate heat for the forest mill sites. However, barks have relatively low heating value especially for wet barks. Therefore, there is a great demand for the developments of suitable and efficient commercial process for converting wasted barks into valuable products [5].
2.4.1 Chemical Composition of Bark

In general, bark has similar cellulose and hemicelluloses content as wood in the fiber portion. However, the chemical composition of bark varies as a function of species, history of disturbance, environmental condition as well as the position of which the bark sample was taken due to its complex heterogeneous structure. Therefore, it is difficult and purposeless to achieve analytical data from different bark samples. The chemical composition of bark can be analyzed using solvent-extraction with subsequent alkali extraction or acid hydrolysis for residue analysis [5]. Bark has approximately ten times more abundant minerals, including calcium, silica and phosphorus, than wood [25]. These minerals are usually referred to the ash content in bark, which makes up to 20% of the bark weight [5]. The rest of the bark components are extractives and remaining lignin, lignans, suberin, phenolic acid, resin acid, fatty acid, non-structural carbohydrates and other phenolic compounds. [4] The bark extractives, which are typically 2-25 wt% in softwood bark and 5-10 wt.% in hardwood bark, are sorted as polar and non-polar materials [5]. The polar extractives, including tannins, polyphenols and glycosides, are typically three to five times more available than nonpolar materials, which include fats, waxes, terpenens, steroids and etc. The amount of lignin in bark is approximately 40-55 wt.%, which is roughly twice more than the lignin content in wood [5]. These phenolic compounds, such as lignin and tannin, contain reactive phenolic moieties that can react toward formaldehyde. Therefore, bark becomes potential partial substitute of petroleum-based phenol in the PF resin synthesis due to its high phenolic content. [4]

2.4.2 Bark Phenolic Compounds: Lignin and Tannins

2.4.2.1 Lignin

Lignin is a natural polymer found in the secondary cell walls of plants and functions as a cell-wall component for bonding cells in stems and provide stems with desirable rigidity and resistance. As mentioned above, lignin is the most abundant component in bark, which typically accounts for up to 55% of the bark’s weight. Lignin is one of the major polymeric components in bark, which is a highly cross-linked, three-dimensional
phenolic polymer with repeating phenyl propane units linked by carbon-carbon or ether bonds with phenolic and alcoholic hydroxyl groups. The lignin fraction in bark can be depolymerized upon heating to form monomeric and oligomeric phenolic compounds. Both softwood and hardwood bark can be used as feedstock in the production of lignin-derived phenolic compounds for the manufacture of phenolic resins. Softwoods contain mostly guaiacol with one methoxy group attached to the phenolic ring, whereas hardwoods are mainly composed of syringol with two methoxy groups in the ortho position. Therefore, softwoods generally yield more reactive phenolics due to the fact that guaiacol has one extra site available for polymerization. The lignin of softwoods is predominantly resulted from the dehydrogenative polymerization of coniferyl alcohol; however, the hardwood lignin is derived from the polymerization of a mixture of coniferyl and sinapyl alcohol. Consequently, softwood barks contain higher lignin contents than hardwood barks. The chemical structures of syringol, guaiacol, sinapyl alcohol and coniferyl alcohol are illustrated in Figure 2.9 [26-27].

![Chemical structures of syringol, guaiacol, sinapyl alcohol and coniferyl alcohol](image)

**Figure 2.9.** Chemical structures of syringol, guaiacol, sinapyl alcohol and coniferyl alcohol [26].

### 2.4.2.2 Tannin

Tannin is an astringent, which can be found in the polar extractives of the bark that bonds with protein. Tannin has been extensively used in leather industry to convert animal hides into leather due to their strong ability to interact with proteins and carbohydrates. Tannins are polyphenolic in nature; therefore, they are considered as a new alternative renewable raw material for phenolic resins production. The typical tannin content in dry bark varies between 2 –40%. Tannins can be generally classified into two types: hydrolyzable tannins and condensed tannins [20, 28].
2.4.2.2.1 Hydrolyzable Tannins

Hydrolyzable tannins can be considered as the mixture of polyesters of gallic and digallic acid derived from glucose and simple phenols such as pyrogallol and ellagic acid [29]. They can be extensively found in the bark extractives from chestnut, myrabalans and divi-divi. Hydrolyzable tannins can be further categorized into gallotannins and ellagittannins. Gallotannins are the simplest hydrolyzable tannins, which are polygalloyl esters derived from glucose. Gallotannins can be converted to gallic acid and its derivatives upon acid hydrolysis (Figure 2.10). The polygalloyl ester chains in gallotannins are formed by depside bonds with a phenolic hydroxyl group, which can be more easily hydrolyzed by weak acid compared to an aliphatic hydroxyl group. Hydrolysis with methanol in weak acid can only break depside bonds but not ester bonds; therefore, strong mineral acid and methanol are used to methanolyze both depside and ester bond under heating to produce the core polyol and its galloyl ester groups. Then, gallotannins can undergo intermolecular oxidative coupling of galloyl groups to yield ellagittannins. The ellagittannins are esters of hexahydroxydiphenic acid (HHDP), which can release ellagic acid and valonic acid under acid hydrolysis (Figure 2.11). Both gallic acid and ellatic acid are significant polyphenolic acids in tannins and have been successfully used to partially substitute phenol, up to 50%, in phenol-formaldehyde resin production [28 – 30].

![Figure 2.10. Conversion of gallotannins to gallic acid upon acid hydrolysis.](image1)

**Figure 2.10.** Conversion of gallotannins to gallic acid upon acid hydrolysis. [30]

![Figure 2.11. The ellagittannins are esters of hexahydroxydiphenic acid (HHDP), which releases ellagic acid and valonic acid under acid hydrolysis.](image2)

**Figure 2.11.** The ellagittannins are esters of hexahydroxydiphenic acid (HHDP), which releases ellagic acid and valonic acid under acid hydrolysis [30].
2.4.2.2 Condensed Tannins

The monomers of condensed tannins are mainly composed of repeating flavonoid units (Figure 2.12), which are flavan-3-ols (catechins) and flavan-3,4-diols (leucoantocyanidins). The repeating flavonoid units contain two phenolic rings, A-rings and B-rings, which are connected by a heterocyclic ring. The remaining portions of the tannin monomer are small amount of polysaccharides and sugars. The condensed tannins are existed as polymers with average degree of condensation of 4 to 12 flavonoid units. The condensed tannins do not undergo hydrolysis, but react with formaldehyde under strong acidic condition based on the Stiasny reaction [29].

![Figure 2.12. Structure of flavonoid][29].

Condensed tannins and their flavonoid precursors are widely distributed in nature and can be extensively found in the wood and bark of various tree species. These tannins can be acquired from extracts of wattle or mimosa bark, quebracho wood, hemlock bark, sumach and pine. The large amount of condensed tannins in these tree species ensure large scale of industrial tannin extraction to give approximately 200,000 tons of tannins production per year, which constitutes more than 90% of total world manufacture of commercial tannins. [29]

In mimosa bark extract, condensed tannins have three major polyphenolic patterns represented by different flavonoid structure. The primary polyphenolic pattern is the flavonoid unit with resorcinol A rings and pyrogallol B rings, which represent about 70% of the total tannins content in mimosa bark. The secondary pattern, about 25% of total mimosa bark tannin fraction, is a parallel pattern to the primary pattern with resorcinol A rings and catechol B rings. The remaining portion of tannin extract is called
“nontannins”, which consist of carbohydrates, hydrocolloid gums and small amount of amino and imino acid. The condensed tannins extracts from the barks of quebracho, wattle, hemlock and Douglas fir have similar polyphenolic patterns. However, condensed tannins in pine bark extracts have totally different polyphenolic patterns, which the dominant flavonoid unit has phloroglucinol A rings and catechol B rings and the minor flavonoid unit has phloroglucinol A rings and phenol B rings. [29]

2.5 Reactivity of Bark Phenolic Compounds towards Formaldehyde

2.5.1 Reactivity of Lignin towards Formaldehyde

Due to the phenolic nature of lignin polymer, lignin derivatives can be used to partially replace phenol to react with formaldehyde in the production of phenol-formaldehyde (PF) resins, which are utilized as adhesives in plywood, particleboard and wafer board. The hydrobenzyl alcohol groups and sulfonic acid groups on the α-carbon of the aromatic ring of the phenyl propane unit react with the atomic nuclei from the vicinal phenyl propane unit under strong acidic condition to produce diphenylmethanes, which is the same as the diphenylmethane unit in the phenolic resin synthesize from phenol and formaldehyde. Therefore, lignin can react with formaldehyde to form cross-linking structure in the same manner as synthetic PF resin [27, 31]. However, lignin is less reactive toward formaldehyde compare to phenol because of the difference in structures between phenol and lignin. As shown in Figure 2.13 below, phenol has five vacant positions on the aromatic ring with no substituents on ortho- and para- position around the hydroxyl group. In reacting with formaldehyde, the aromatic hydroxyl group on phenol can be cross-linked with vicinal aromatic hydroxyl group by forming methylene bridges on ortho- and para- sites. While in phenolic structure of lignin, there is only 35 free phenolic hydroxyl group and 5 benzylic hydroxyl groups per 100 C9 repeat units. The para-positions on the aromatic rings of lignin are substituted by the propyl chain of the 1-propylphen-4-ol structural units, which block and reduce the amount of available sites for lignin to react with formaldehyde. This reduces reactivity of lignin toward formaldehyde. Therefore, lignin can only partially replace phenol, approximately 40 - 70wt%, in PF resin formulation. Moreover, the open ortho position on softwood lignin promotes the
cross-linking reaction between softwood lignin and formaldehyde, which gives softwood lignin higher reactivity toward formaldehyde than hardwood lignin. [27]

![Cross-linking reaction between softwood lignin and formaldehyde](image)

**Figure 2.13.** Reaction of phenol towards formaldehyde [27].

### 2.5.2 Reactivity of tannin towards Formaldehyde

Hydrolyzable tannins have low reactivity towards formaldehyde due to its low nucleophilicity and low-level substitution of phenol. However, condensed tannins with repeating flavonoid unit have high reactivity toward formaldehyde to form polycondensates with rigid structure and molecular weight. The nucleophilic centers on the A ring of the condensed tannin’s flavonoid unit are more reactive than those on the B ring due to general activation of the nucleophilic centers in B ring caused by the vicinal hydroxyl substituents. In cross-linking with formaldehyde, polymerization of tannins occurs by forming methylene bridge linkages at reactive sites, mostly A rings, on the flavonoid unit. For all the flavonoid units, either one of position 6 or 8 on A rings are the reactive positions according to the type of tannins. For upper terminal flavonoid molecules, both position 6 and 8 on A rings are reactive sites for polymerization. The reactivity of A rings of mimosa and quebracho tannins towards formaldehyde is comparable to that of resorcinol. B rings react with formaldehyde only under strong alkaline condition with pH >10. However, the reaction rate of A rings and formaldehyde becomes uncontrollable fast at such high pH value causing the undesirable short pot-lives of tannin-formaldehyde resin. In general, only A rings on the tannin flavonoid unit react with formaldehyde to form cross-linking structure in tannin adhesive. The problem of tannin-formaldehyde reaction is that the mobility of tannin molecules is retarded at a low level of condensation with formaldehyde, due to size and shape of tannin molecules, which causes the distance between available reactive sites become too large for methylene bridge linkages to form. As a result, the incomplete polymerization would happen and cause weakness in the synthetic tannin resin [29].
2.6 Novolac PF Resins Prepared from Bio-based Phenol and Its Applications

Biomass can be converted to bio-fuel and bio-based chemicals through biochemical and thermochemical conversions. Biochemical conversion involves the use of either enzymatic or chemical process to break down the biomass into sugars and then converts sugar to ethanol through fermentation. Thermalchemical conversion of biomass includes gasification, pyrolysis and liquefaction. In gasification, lignocellulosic biomass are heated at extremely high temperature, at 1000ºC, and converted into synthetic gas, which are mainly composed of CO and H₂. In pyrolysis, biomass is heated in the absence of oxygen and thermally degraded to obtain charcoal, bio-oil and fuel gas. Liquefaction involves the use of organic solvents, such as phenol, polyhydric alcohols, ethylene carbonate and etc., to decompose lignocellulosic biomass into lower molecular weight substance through solvolysis in order to improve the reactivity and flowability of biomass. This paper will focus on reviewing novolac PF resins prepared from bio-based phenol using pyrolysis and liquefaction process [3].

2.6.1 Novolac PF Resins from Pyrolysis Oil

Pyrolysis is one of the most important thermochemical conversion methods for the production phenolic resins from biomass. Each component of the biomass, such as cellulose, hemicelluloses, lignin and other organic compounds, can be degraded by different mechanisms during the pyrolysis process. The reaction temperature, heating rate and pressure inside reactor can affect the pyrolysis rate and decomposition efficiency [32]. The final product of the process is the pyrolysis oils, also known as bio-oils, which contain large amount of water with roughly up to 45% of oxygen, followed by approximately 10wt% of hydroxyacetaldehyde and about 8wt% of acetic and formic acid [26]. The fast pyrolysis and vacuum pyrolysis are two most common pyrolysis processes. The vacuum pyrolysis is usually used to produce phenolic resin precursors from biomass for phenol substitution in resole resin formulation. Therefore, this review will investigate the fast pyrolysis oil as phenol substitutes for novolac resin synthesis.
Fast pyrolysis is a recently developed thermochemical conversion technology for phenolic resin production. Biomass is rapidly heated to moderate temperature between 400 and 600ºC without the presence of oxygen and decomposed into large amount of vapors with aerosols and some charcoal during the fast pyrolysis process. [30] This technology can produce up to approximately 75wt% liquid yields on a dry basis woody biomass with low ash content; however, the liquid production requires short vapor residence times, usually less than 5s, in order to eliminate secondary reaction and ensure the rapid condensation of pyrolysis vapors to obtain the pyrolysis oil product. [26]

Chum et al. [26] synthesized novolac and resole resins from the pyrolysis oils produced from hardwood, softwood and bark. Fast pyrolysis experiments were conducted in a vortex reactor with 10-20 kg/h capacities and operating temperature at 480-520 ºC in order to achieve the desirable yields of pyrolysis oil, which is typically 55wt% on a dry basis. The extremely high heat transmission from heat fluxes to biomass depolymerizes polymers into monomers and oligomers inside the reactor. The pyrolysis process was completed with a series of condensation at different temperatures to condense the vapor product and acquire the pyrolysis oil. The first condensation stage used a cyclonic condenser to condense the vapor products with chilled water at 20 ºC. A vertical vortex tube was utilized in the second condensation stage to cool the product gases to 2ºC. The last stage was a carboy immersed in a mixture of dry-ice and propanol bath to further condense all the vapors to -17ºC. The remaining gas and aerosol stream was further removed by a coalescing filter. The fraction of pyrolysis oil with rich reactive phenolics was acquired after the second stage and treated with organic solvent and basic solution to recover phenolics and neutrals on a dry feed basis of 20-25 wt%. The fraction containing phenolic and neutral components was used in novolac resin synthesis to substitute 50% of phenol in the original formulation, which gives the synthesized novolac resin a shorter gel time than commercial plywood resins. The author also found that the aldehyde groups in the neutral components could be used to partially substitute the formaldehyde used in the resin synthesis with a reduction of approximately one-third of the amount of formaldehyde used in normal formulation at a phenol substitution level of 50%.
Xu et al. [33] synthesized high-ortho novolac resins (PPF) using water insoluble fraction from biomass pyrolysis oil to partially substitute phenol and react with formaldehyde in a two step synthesis reaction. The condition and process for the pyrolysis was not mentioned in the paper. The bio-oil obtained from pyrolysis was first separated into water soluble and insoluble fractions through fractionation, where 100 g of water was added to 200 mL bio-oil (approximately 232g) dropwisely with constant stirring to obtain 73g water-soluble fraction and 82.4g water-insoluble fractions. By analyzing the main components in original bio-oil and in water-insoluble fractions, it was indicated that water-insoluble fractions contain higher amount of phenolic compound. Therefore, the author used water-insoluble fractions from phenolic-rich pyrolysis oil to partially substitute phenol, 10, 20, 30 and 40wt% in total amount of phenol used, in novolac resin synthesis with HCl and Zn(Ac)$_2$ catalysts. The results have shown that as the amount of water-insoluble fraction increased, the reaction time and amount of catalyst used were increased in order to maintain the desirable soft point in the novolac resin product. By conducting the GC-MS analysis on the water-insoluble fractions of the pyrolysis oil, the author found that the major components in the water-insoluble fractions are oligomeric lignin derivatives. The ortho- and contra- positions in these lignin-derived components were substituted by methyl, methoxy, propenyl, ketones, and aldehyde groups. Thus, phenol substituted with these water-insoluble fractions was less reactive towards formaldehyde in comparison to pure phenol due to the lack of reactive sites in its molecular structure. The non-phenolic components in the pyrolysis oil also reduce its reactivity toward formaldehyde. Therefore, longer reaction time and more catalyst loading is essential to maintain the desirable soft point of novolac resin when increase the amount of insoluble fraction in phenol substitution. Moreover, the author mentioned that the future research would be focus on extracting phenol rich compounds from water insoluble fraction in phenol substitution.

### 2.6.2 Novolac PF Resins from Modified Ligninosulfonate

As mentioned above, lignin is a highly cross-linked and three-dimensional phenolic polymer with phenolic hydroxyl groups. Therefore, lignin can be used as phenol
substitute in phenol-based resin or converted into phenolic precursors for PF resins synthesis. Lignin is largely available as by-product from pulp and paper industry. However, most of lignin from the pulp and paper industry is consumed in the Kraft process to recover the reagents used in pulping. Lignosulfonate is a lignin-derived chemical obtained from the sulphite process in wood pulping as a by-product, which is largely available with a production amount of approximately 6% of total lignin production from the pulp and paper industry. Therefore, lignosulfonate, the most abundant industrial lignin, is a good alternative to lignin used in the industrial production of PF resin. According to the previous study from Calve et al. and Allan et al. [34], the ammonium lignosulfonates are the most adequate substitute for phenol in phenolic resin formulation because resin synthesized using ammonium lignosulfonates have better properties. Due to the low reactivity of lignosulfonates with phenol and formaldehyde, the direct use of ligninosulfonates as phenol substitute is not favorable in industrial application because of the extremely long process time and high temperature. Lignin modification should be done in prior to resin synthesis in order to activate ligninosulfonate. Phenolation and methylation are the two most common structural modification processes to increase the reactivity of ligninosulfonate towards formaldehyde [34–35].

M. V. Alonso et al. [34] modified lignosulfonates under the phenolation process to acquire a suitable material for novolac PF resin synthesis. The phenolation process was chosen because both phenolation process and novolac resin synthesis happen under acidic condition and the modified lignosulfonate mixture can be directly incorporated into novolac resin formulation without removing unreacted phenol from the phenolated product. The ammonium lignosulfonate from spruce wood was used in this phenolation study. During the phenolation process, the ammonium lignosulfonates and phenol were dissolved in 600ml of deionized water and the reaction happen under the catalysis of oxalic acid. The phenolated mixture was then precipitated using concentrated acetic acid and washed with ethyl ether. The phenolation of ammonium lignosulfonates with phenol was favored at high phenolation temperature, long reaction time and low lignosulfonate concentration with optimum phenolation condition at 120°C for 160min with 30%
The results have been indicated that lignosulfonate condensation became more significant at higher lignosulfonate concentration, which require high temperature to enhance phenolation. Based on the FTIR, the adduct fragmentation occurred due to the ether groups cleavage as the reaction proceeded. According to the $^1$H NMR analysis, the addition of lignosulfonate to the ortho-position is predominant over the para-position on the aromatic ring of phenol during the structural modification. The fragmentation of lignosulfonate caused both the molecular weight and polydispersity of phenolated lignosulfonates to decrease after the phenolation process, which is favorable for the resin synthesis. And the decrease becomes more obvious at high temperature and long reaction time. In this study, the author has proven that the phenolation with longer time (160min) can decrease the molecular weight to a desirable range, which the modified ammonium lignosulfonate becomes more favorable for the phenolic resin synthesis. However, there is no further study on the resin synthesis using phenolated lignosulfonate. Therefore, the physical and mechanical properties of the phenolated lignosulfonate substituted novolac resin are unknown.

Methylolation is another effective structural modification process for lignosulfonates with less expensive installation cost. J. M. Perez et al. [35] formulated lignin-novolac resins using methylation-modified softwood ammonium lignosulfonates to partially substitute phenol in resin synthesis for textile felts application. Although, the detail procedure of methylolation of lignosulfonates was not discussed, the reaction mechanism of lignosulfonates with phenol and formaldehyde in acidic condition was proposed in the paper (Figure 2.14). Due to the presence of lignosulfonates, the sulfonate group is attached to the $\alpha$-carbon on the lateral chain of the phenyl propane unit. The lignosulfonates may react with itself or phenol to form linkage on the $\beta$-carbon of the lateral chain. The FTIR and NMR spectroscopies demonstrated that the methylolated lignin-novolac resin acquired a more complicated structure from the functional groups of the substituted ammonium lignosulfonate compared to the commercial novoalc resin. But these functional groups with high variety favor the curing process of the resin. Furthermore, the phenol, formaldehyde and water content, softening point and flow
distance value of methylolated lignin-novolac resin was in the specification range required for the textile felt applications.

![Proposed mechanism of lignin-novolac resins synthesis substituted with lignosulfonates](image)

**Figure 2.14.** Proposed mechanism of lignin-novolac resins synthesis substituted with lignosulfonates [35].

### 2.6.3 Novolac PF Resins from Liquefied Biomass

There are generally two types of liquefaction for the thermochemical conversion of biomass into phenolated materials that can be used as phenol substitute in resin synthesis. The first one is called the direct liquefaction, which is similar to the pyrolysis but at elevated temperature and 5-10 MPa pressure. The second type of liquefaction uses organic solvent to dissolve biomass at moderate temperatures range from 100-250 °C with or without using acid catalyst. During this type of liquefaction, the organic solvent decomposes the lignocellulosic biomass to substances with low molecular weight through
solvolysis in order to enhance the flowability and reactivity of the biomass. The second method is commonly used to liquefy biomass for different resin synthesis [3].

Liquefaction of biomass is mostly conducted under catalysis of acid in order to reduce the reaction temperature and increase the liquefaction extent. As mentioned above, novolac is a thermoplastic phenol-formaldehyde resin, which is synthesized under acidic condition with excess amount of phenol. Thus, the use of acid-catalyzed liquefied biomass is preferable in novolac resin synthesis. During the liquefaction, the ground fine biomass particles were liquefied using designed amount of phenol and acid catalyst. The liquefied biomass was then diluted using methanol and filtered to remove un-liquefied residues. After the filtration, the methanol and un-reacted phenol inside the liquefied biomass filtrate was removed through reduced-pressure evaporation. After above procedures, the liquefied biomass can be either used directly as a novolac-like resin or further react with formaldehyde through condensation to form novolac PF resin [3].

Lin et al. [36] synthesized novolac-like liquefied wood resin using phosphoric acid as liquefaction catalyst. Lin’s group found that phosphoric acid is an adequate catalyst for liquefaction of wood. During the liquefaction process, wood meals of Birch were first ground to reduce particles size to 20-200 mesh. The fine wood particles were then mixed with phenol and acid catalyst at designated ratios for liquefaction. After the general post-liquefaction process, a novolac-like resin was obtained from liquefied wood by removing free phenol through reduced-pressure evaporation at 180°C. It was reported that the increase in liquefaction temperature, liquefaction time, catalyst loading and phenol to wood ratio caused the increase in amount of phenol reacted and combined with liquefied wood components. Studies have shown that the flow properties of the liquefied wood obey the Ostwald de Waele power law equation with a pseudo-plastics behavior and strongly depend on the amount of reacted phenol in the liquefied wood. Moreover, the flowing temperature, activation energy, and zero shear viscosity of liquefied wood increased as the amount of combined phenol in liquefied wood increased.
Lin et al. [37] conducted a comprehensive study on the molding of synthesized novolac-like liquefied wood resin. The molding compounds was prepared using 37.7wt% of novolac-like liquefied wood resin with 49.5wt% of wood powder as the filler, 9.4wt% HMTA as the curing agent, 2.4wt% Ca(OH)$_2$ as the accelerating agent, and 1wt% zinc stearate as lubricating agent. It was proven that novolac-like liquefied wood resin using phosphoric acid as catalyst can be molded successfully and has comparable curing reactivity as the conventional novolac molding when the same molding conditions were used. The mechanical and physical properties of the molding object using liquefied wood resin was tested and compared to the conventional novolac molding products. The results from flexural test of molding sample indicated that the flexural strength of molding product was improved as the amount of wood filler in molding compound and the content of reacted phenol in liquefied wood resin increased. The mechanical properties of liquefied wood resin moldings are comparable to the reference commercial novolac moldings when the combined phenol in the liquefied wood reached 75%. The water-sorption test indicated that liquefied wood resin moldings are more hydrophilic with higher water-diffusion coefficient than the reference commercial novolac moldings. However, the hydrophillicity of the moldings decreased as the amount of combined phenol in the liquefied wood increased. Moreover, the micrographs obtained from Scanning Electronic Microscopy (SEM) showed that liquefied wood resin moldings are more compatible with wood fillers and achieved a better mechanical reinforcement by wood filler than conventional novolac moldings.

Without removing the un-reacted phenol from the liquefaction, formaldehyde is added to react with the remaining phenol in liquefied wood through condensation in order to obtain liquefied wood phenol formaldehyde (LWPF) novolac resin. Lin et al. [38] prepared a phenolated wood/phenol/formaldehyde co-condensed novolac resin using phosphoric acid and oxalic acid as catalyst in a two-stage procedure, which the first stage is the liquefaction of wood in phenol under the catalysis of acid and the second stage is the condensation of the phenolated wood from first stage with formaldehyde to convert un-reacted phenol to resin components. The formaldehyde to phenol ratio was chosen to be 0.8/1 where the non-reacted phenol in phenolated wood was used to indicate the
amount of formaldehyde used. It was found that this two-stage procedure was able to achieve 94% conversion of un-reacted phenol into final resin product when 3.8% of phosphoric acid was used during the liquefaction stage. While using oxalic acid as catalyst in wood liquefaction, an extra amount of oxalic acid was added during the subsequent condensation reaction to improve the conversion of un-reacted phenol into resin component. The flow temperature and melt viscosities of the co-condensed LWPF novolac resin synthesized using both phosphoric acid and oxalic acid catalysts were lower than liquefied wood novolac resin and comparable to the commercial novolac resin. The enhanced mechanical properties and significantly higher flexural strength was observed from the moldings from the LWPF novolac resin in comparison to moldings made from the directed liquefied wood resin and even superior to the commercial novolac resin moldings in some extents. Therefore, this two-stage procedure is a promising technique for preparing LWPF novolac resin.

W. Lee and Y. Chen [39] liquefied the wood of Japanese cedar (Cryptomeria japonica) in phenol using sulfuric acid and hydrochloric acid as catalyst follow with a subsequent condensation reaction with formaldehyde to obtain LWPF novolac resin. At the beginning of the study, Lee and Chen hypothesized that all the reactive sites on wood components, reacted phenol and non-reacted phenol could react with formaldehyde to synthesize LWPF resin. Therefore, the entire phenolated wood was considered as “phenol” and used as basis to determine the phenol to formaldehyde ratio. However, it was found later that the phenolated wood were cured too fast into insoluble and infusible resin product in an uncontrollable manner by using the molecular weight of the entire phenolated wood to determine the amount of formaldehyde used in the resin synthesis. It was more feasible to use the amount of remaining non-reacted phenol from liquefaction to determine the phenol-to-formaldehyde ration in resin synthesis. It is worth mentioning that Lee and Chen reported the reaction of liquefied Japanese cedar with formaldehyde was exothermic with the formation of a solid-form thermoplastic novolac resin. The heat generated from the reaction can heat the system to 76°C when using sulfuric acid catalyst and 106°C when using hydrochloric acid catalyst without external heat supply, giving the yield of novolac LWPF resin of 85.4% and 67.2%, respectively. Moreover, both acid-
catalyzed LWPF novolac resin can produced good-performance molding using hot-press at 200 °C for 10mins with novolac/wood filler/HMTA/Zinc stearate weight ratio of 60/30/10/1.

Pan et al. [39 – 41] synthesized liquefied wood/phenol/formaldehyde (LWPF) resins using Chinese tallow tree wood and oxalic acid as catalyst. The Chinese tallow tree wood was dried at 105°C in the oven to reduce the moisture content to 3-5% and ground into 20-200 mesh in prior to the liquefaction. The liquefaction of Chinese tallow wood was conducted in two types of reactors, which are the atmospheric three-neck flask and the sealed Parr reactor, using 5% oxalic acid as catalyst based on the amount of phenol used. Three phenol to wood ratios, which are 1/1, 2/1 and 3/1 (w/w), and two liquefaction temperatures, which are 150 and 180 °C, were studied during the liquefaction stage. The liquefied wood/phenol mixture obtained from the liquefaction was further reacted with formaldehyde at a phenol to formaldehyde molar ratio of 1/0.8 and additional 7wt% of oxalic acid, based on the initial amount of phenol used, at 105°C for 80 minutes. The product obtained from the co-condensation reaction was first diluted with acetone and then filtered to remove the wood residue under the vacuum. The final LWPF resin was obtained by evaporating acetone under reduced-pressure. It was reported that the LWPF resin synthesized using the liquefied wood from the Parr reactor has lower molecular weight than those made from the atmospheric three-neck flask. The average molecular weight of atmospheric three-neck flask liquefied wood synthesized LWPF resin increased as the P/W ratio increased; while the average molecular weight of LWPF resin decreased with increasing P/W ratio when the resin made from Parr reactor liquefied wood. The results of FTIR spectroscopy showed that the LWPF resin has similar spectra as the commercial novolac resin with a major difference at the 1800-1600 cm⁻¹ regions, which is responding to the partial phenol substitution by liquefied wood component during the resin synthesis.

Pan et al. [39 – 41] also studied the physical and mechanical properties of the bio-composite made from the synthesized LWPF resin. The LWPF resin with 2/1 phenol/wood ratio was chosen as the matrix and the Chinese tallow wood powder with
20 mesh in size was chosen as the filler to prepare the bio-composite using a single-opening laboratory hot-press at 185°C for 3 minutes. The compositions of the bio-composite are 37.7% LWPF resin, 9.4% Hexamine, 2.4% Calcium Hydroxide, 1% Zinc Stearate and 49.5% Wood filler. Both flexural and tensile strengths of the composites were tested; however, the data was not consistent as there were no apparent trends observed due to the complex composition of the LWPF resin and/or flaws in the composite test specimen. Moreover, the dimensional stabilities of the composite were studied by the soaking and boiling tests. The test specimens were soaked in water and the thickness of the specimen was measured every 24 hours for total 96 hours during the soaking test. For the boiling test, the composite test specimens were boiled in water for 8 hours with the thickness measurement in every two hours. The results showed that composite made from LWPF resin containing the liquefied wood component from sealed Parr reactor had higher thickness swelling than those made from LWPF resin with liquefied wood component obtained from the atmospheric three neck flask and composites prepared from LWPF resin under higher liquefaction temperature yielded higher thickness swelling for both soaking and boiling test. In the paper, the author mentioned that the liquefaction conducted in the sealed Parr reactor and/or under higher temperature had greater liquefaction extent and therefore the composites prepared from the LWPF resins using liquefied wood from the Parr reactor and/or under higher liquefaction temperature contained more wood component, which were more hydrophilic and had poorer dimensional stabilities.

Alma [42] investigated the tensile properties of molding composites made from the phenolated barks under sulfuric acid catalysis for various tree species (Pinus brutia Ten., Cedrus libani, Eucalyptus camaldulensis, Robina pseudoacacia, Castanea sativa, and Quercus cerris). 20 grams of tree bark was grained into 20-80 mesh and reacted with 40 grams of phenol and sulfuric acid catalyst (0.5, 1, 2, and 4% based on phenol weight) in a separable four-necked glass resin cattle at 130°C for 60 min. At the end of the phenolation process, the reaction products were diluted with methanol and then filtered to remove bark residue using a glass-fiber filter. Magnesium oxide was used to neutralize the remaining sulfuric acid in the product. The methanol was then evaporated at 50°C.
under vacuum. The final condensed phenolated bark was obtained in a solid form after distilling the free phenol from the solution under a reduce pressure of 25mmHg at 180°C for 1 hour. The phenolated bark was dissolved in acetone and uniformly mixed with HMTA, zinc stearate, calcium hydroxide and wood powder. The mixture was oven-dried at 70°C for 1 hour to evaporate acetone in prior to molding. The dried molding compounds were then molded into test specimens with a dimension of 4×10×80mm at 190°C for 5min under 40MPa in a die. A commercial novolac resin was used as reference in this study. The author found that the tensile strength of phenolated bark-based molding composite for all the bark species increased as the catalyst concentration increased from 0.5 to 2% and then decreased if catalyst concentration continued to increase. The results showed that the molding composite made from phenolated pine bark has the highest values in all tensile properties (tensile strength, Young’s modulus and Elongation) while the molding composite prepared with phenolated acacia bark has the lowest values in all tensile properties for all catalyst concentrations. Moreover, it was found that the phenolated bark composite has comparable tensile properties and better compatibility of the phenolated bark matrix with the wood filler in comparison to the reference composite prepared with conventional novolac resin and wood filler.

2.7 Conclusions

This chapter first reviewed the general background of traditional phenol formaldehyde resins synthesis, their commercial applications and the concerns in regarding to the current production of phenol formaldehyde resins. The second part of this chapter provided a detail literature review from previous studies on obtaining partial phenol substitute from lignocellulosic biomass (wood, bark and etc.) through different techniques, such as pyrolysis, phenolation, and liquefaction, to prepare the novolac PF resin from bio-based phenol and the applications of these bio-based PF novolac resin. Wood, as one of the major lignocellulosic biomass, contains large amount of phenolic compounds, lignin and tannin, which has similar phenolic structure as phenol. Tremendous researches have studied the use of phenolated wood as phenol substitute in PF resin synthesis. Barks, which are largely available as low-cost residue from forest mills sites and currently treated as waste, has very similar chemical composition and
phenolic content as wood. Previously, Y. Zhao et al. [17 – 18] have successfully synthesized PF resol resins using the liquefied mountain pine beetle infested lodgepole pine bark under alkaline conditions. Studies have found that the synthesized PF resol resins with liquefied MPB infested lodgepole pine bark component demonstrated comparable dry and wet bonding strength to a commercial oriented strand board (OSB) face layer PF resol resin. However, no previous studies have been reported on incorporating liquefied MPB infested lodgepole pine barks in the novolac PF resin synthesis. Limited researches have investigated the effects of the resin formulation on the curing behavior and thermal stability of the synthesized bio-based novolac PF resins and the application of these bio-based novolac PF resins in thermal molding. Hence, it would be highly beneficial to the forest industry if these MPB infested lodgepole pine barks could also be converted into alternative substitutes for petroleum based phenol and partially replace phenol in the PF novolac resin production.

The following chapters describe my thesis study on utilizing liquefied MPB infested lodgepole pine bark component as partial phenol substitute to formulate a bio-based novolac PF resin. The bio-based phenol substitutes were acquired using the bark phenol liquefaction methods under the catalysis of either sulfuric acid or hydrochloric acid. The liquefied MPB infested lodgepole pine bark components were characterized to investigate the impact of catalyst types on the bark phenol liquefaction. The liquefied bark components were directly used as partial phenol substitute to react with formaldehyde under acidic condition to synthesize the bio-based PF novolac resins. Two types of liquefied bark PF novolac resins were synthesized and tested to compare with a lab-made control novolac resins, which does not contain liquefied bark components, in terms of resin characteristics and properties. The applications of the synthesized bio-based novolac PF resin in thermal molding were explored. The characteristics and performance of the synthesized bio-based novolac PF resins and its molding composites were investigated in order to study the impact of liquefied MPB infested lodgepole pine bark components and catalyst types on the resin properties and the performance of corresponding molding composites and fulfill the knowledge gap in the current study of the adhesive application of MPB infested lodgepole pine barks.
Chapter 3

Experimental Approach

This chapter covers the experimental methods for bark phenol liquefaction, liquefied bark PF novolac resin synthesis, preparation of molding composites using liquefied bark novolac resins and the techniques for characterizing the acid-catalyzed liquefied bark products, bio-based liquefied bark PF novolac resins and its molding composites.

3.1 Bark Phenol Liquefaction

Mountain pine beetle (MPB, Dendroctonus ponderosae Hopkins) infested lodgepole pine (Pinus contorta Dougl.) barks were liquefied in phenol at a set temperature of 150°C for 120 min with a phenol to bark weight ratio of 3:1. The bark phenol liquefaction was conducted under the acid catalysis of either sulfuric acid or hydrochloric acid, which the resulting phenol liquefied bark was denoted as LB-S and LB-C respectively. The catalyst loading was 3% based on the phenol weight. After the reaction, the liquefied products were cooled down to room temperature and diluted with excessive amount of methanol.

3.1.1 Measurement of Liquefied Yield

The loss of gaseous products was not expected during the liquefaction process since the liquefaction was carried out at moderate temperature with the use of condenser and the liquefied products have low volatility. Therefore, the yield of bark liquefaction can be directly indicated from the residue ratio. The diluted liquefied products were filtered using Millipore filter paper to separate the methanol insoluble residue. The unliquefied bark residues were dried in the oven at 105°C to a constant weight for determining the residue ratio. The residue ratio was calculated using the below equation:

\[ R = \frac{W_r}{W_o} \times 100\% \]  

(1)

Where R is the residue ratio of the bark phenol liquefaction reaction (%), \( W_r \) is the oven-dry weight of unliquefied bark residue after liquefaction (g), and \( W_o \) is the original oven-dry weight of bark before liquefaction (g).
3.1.2 Measurement of Free Phenol Content

The free phenol content in the liquefied bark fraction was analyzed using a Perkin Elmer HPLC with a UV detector set at a wavelength of 254nm. 25 µl of sample was injected into the injection port with 0.45 µm PTEE pre-filter and was eluted with a mobile phase of 65% methanol and 35% water at a rate of 1.0 ml•min⁻¹ through a C18 reverse phase column with a dimension of 4.6 mm × 250 mm. An external standard calibration in the concentration range of 50-2000 ppm (R² = 0.99) was used to quantify the free phenol peak. The free phenol peak appeared at approximately 1.8 min and the free phenol content of the liquefied bark fraction was calculated by the following equation:

\[
F_{Ph} = \frac{W_{FPh}}{W_o + W_{ph} + W_r} \times 100\% \tag{2}
\]

Where FPh is the free phenol content in the liquefied bark fraction (%), W_{FPh} is the weight of free phenol after the liquefaction (g), W_o is the original oven-dry weight of bark before liquefaction (g), W_{ph} is the weight of phenol before liquefaction (g), and W_r is the oven-dry weight of unliquefied bark residue after liquefaction (g).

3.1.3 Chemical Composition Analysis

Chemical composition analysis of the unliquefied bark residues includes measurements of the holocellulose, alpha-cellulose, and lignin content. The unliquefied bark residues were first separated from the liquefied products using the ASTM D1105-96 method. Zobel et al.’s method [43] was used to analyze the holocellulose and alpha-cellulose contents. Acid-insoluble lignin content was analyzed according to ASTM D1106-96 method.

3.2 Formation of Liquefied Bark Containing Novolac Resins

The excess methanol in the diluted liquefied bark was first removed under reduced pressure. The obtained liquefied bark component was then reacted with formaldehyde under acidic condition to synthesize liquefied bark novolac phenol formaldehyde resins. The liquefied bark novolac PF resin with sulfuric acid-catalyzed liquefied bark component was denoted as liquefied bark novolac PF resin S (LBPF-S). The liquefied

40
bark novolac PF resin derived from the hydrochloric acid -catalyzed liquefied bark component was denoted as liquefied bark novolac PF resin C (LBPF-C).

A calculated amount of liquefied bark was first mixed with HCl acid catalyst and loaded in an atmospheric three-neck flask to be heated to 85 °C. A calculated amount of formaldehyde solution (37%) was added to the mixture drop-wisely during the first 60 min of reaction. After the addition of formaldehyde, the reaction continued at 85 °C for 60 min. The acquired resin products were in solid form and ground into powders for further characterization and experiments. Lab-made control novolac PF resins without bark components (Lab PF) were synthesized using the exact same compositions and procedures as the liquefied bark novolac resin formulation and used as a lab-control reference resin for the further characterizations and experiments.

Three weight ratios of formaldehyde to phenol were used for lab-made control resin formulation, which were 0.35, 0.52, and 0.69, corresponding to equivalent molar ratios of 0.4, 0.6, and 0.8, respectively. The resulting lab-made control novolac resins were denoted as Lab-PF-0.4, Lab-PF-0.6, and Lab-PF-0.8. The weight ratios of formaldehyde to liquefied bark in the LBPF resin formulation were the same as the weight ratios of formaldehyde to phenol in Lab PF control resin formulation. The corresponding liquefied bark novolac resins are denoted as LBPF-S-0.4, LBPF-S-0.6, and LBPF-S-0.8 for sulfuric acid catalyzed liquefied bark novolac PF resin; LBPF-C-0.4, LBPF-C-0.6, and LBPF-C-0.8 for hydrochloric acid catalyzed liquefied bark novolac PF resin.

3.3 Characterization of Liquefied Bark Novolac Resins

3.3.1 Differential Scanning Calorimetry (DSC) Analysis of the Resins

The resin curing behavior was analyzed using Differential Scanning Calorimetry (DSC). Hexamethylenetetramine (HMTA) was used as the curing agent for the novolac PF resins. The weight ratio of novolac resins and HMTA was 10:1. High-pressure pans (DSC-Q1000, TA Instruments, USA) were used in this study for investigating the resin curing behavior. Dynamic scans were conducted at heating rates of 5, 10, 15, and 20 °C/min, starting from room temperature and increasing to 300 °C.
3.3.2 Curing Kinetics

The activation energy was calculated using the Kissinger method [44].

\[
\ln\left(\frac{\varphi}{T_p^2}\right) = -\frac{E}{R T_p} + \ln\left(\frac{A}{E}\right)
\]

(3)

Where, \(\varphi\) is the heating rate (K/s), \(T_p\) is the peak temperature (in Kevin) at the given heating rate, A is the pre-exponential factor, R is the ideal gas constant, and E is the activation energy. For each testing sample, three replicates were conducted. The maximum variation in the onset and peak temperature was less than 1 °C.

3.3.3 Thermal Stability

Thermal gravimetric analyzer (TGA-Q500, TA Instruments, USA) was used for analyzing the thermal stability of the resins. An approximate 10 mg of uncured and cured lab-made novolac resins and liquefied bark novolac resins testing samples was loaded in a platinum pan and heated in the combustion chamber from room temperature to 800 °C at the rate of 10 °C/min under the nitrogen atmosphere.

3.3.4 FTIR of Liquefied Bark, Unliquefied Bark Residues and Liquefied Bark Novolac Resins

FT-IR TENSOR 27 spectrometer (Brock Optics, USA) was used to obtain the FTIR measurements of the liquefied bark fraction, unliquefied residues, and liquefied bark novolac resins with a frequency range of 4,000 – 400 cm\(^{-1}\). Testing samples were prepared using KBr pellet method.

3.3.5 Molecular Weight

Matrix-Assisted Laser Desorption/Ionization-Time-of-Flight/Time-of-Flight spectrometer (MALDI-TOF/TOF, Applied Biosystems, Framingham, MA, USA) was used to measure the weight average molecular weight (\(\bar{M}_w\)), number average molecular weight (\(\bar{M}_n\)), and polydispersity index (\(\bar{M}_w/\bar{M}_n\)) of liquefied bark and liquefied bark novolac resins. The mass spectra were obtained in the low linear mode with a mass range from 60 to 6,000 Da at the laser intensity of 7,000. DHB (2,5 – dihydroxy benzoic acid) was used as the
matrix for the sample preparation. The matrix material was mixed in 50% aqueous ethanol and 0.1% trifluoroacetic acid to obtain matrix solution with a concentration of 10mg/ml. The liquefied bark sample was premixed with the matrix at a volume ratio of 1:4, and then 1 µl of the mixture was added on the MALDI target and dried under air. Each spectrum was collected by the total number of ions from 500 laser pulses. Mane et al.’s [45] methods were used to calculate the average molecular weight and polydispersity index.

3.4 Preparation of Molding Composites from Liquefied Bark Novolac Resins

3.4.1 Materials

The lab-made control novolac PF resins and HCl acid-catalyzed liquefied bark novolac PF resins with formaldehyde to phenol or liquefied bark ratio of 0.6 (Lab-PF 0.6 and LBPF-C 0.6, respectively), which were synthesized from previous experiments, were used as the matrix for molding the composites. The resins were dried and ground into 60 mesh. The maple wood power were sieved to size under 60 mesh and used as filler. The hexamine (HMTA), calcium hydroxide and zinc stearate were used as the hardener, accelerating agent and lubricating agent, respectively. Only LBPF-C resins were chosen to study the application of bio-based liquefied bark novolac PF resins in novolac-molding composite because the H₂SO₄ acid catalyzed liquefied bark novolac PF resins (LBPF-S) were failed to mold into composites. According to our previous study on the resin properties, LBPF-S had a higher molecular weight than LBPF-C, which acquired a higher cross-linking structure through the incorporation of H₂SO₄ acid catalyzed liquefied bark components to the novolac resin formulation. Therefore, LBPF-S were suspected to be partially cured or a partially thermosetted due to its highly cross-linking structure. The Lab-PF-0.6 resins, with no liquefied bark component, were used as a reference.

3.4.2 Preparation of Molding Composites

The molding composites were prepared using three formulas with different resin to filler ratio. The compositions for each formula in regarding to the ingredients and weight ratio of each molding compound were listed in Table 3.1. The wood powder was dried in the oven at 60 °C overnight before mixing with other ingredients. Acetone was added to
dissolve the Lab-PF-0.6 and LBPF-C-0.6 resin powder, and then wood powder, hexamine, calcium hydroxide and zinc stearate were uniformly mixed with the resin solution into a slurry-like mixture. This slurry-like mixture was dried in the oven at 40 °C under vacuum overnight to evaporate acetone. The dried mixture of molding compounds was ground into fine powder in a mortar and ready for molding.

Approximately 15g of molding compound mixture were molded into test specimens at 190 °C for 15 minutes with thickness control of 3mm in a Laboratory Molding Press. The compression-molded test specimens had a dimension of 3 × 19 × 165 mm (thickness × width × length). (Figure 3.1)

<table>
<thead>
<tr>
<th>Molding Compounds</th>
<th>Weight Ratio</th>
<th>Weight Ratio</th>
<th>Weight Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Formula 1 - 7:3</td>
<td>Formula 2 – 5:5</td>
<td>Formula 3 – 3:7</td>
</tr>
<tr>
<td>LBPF-C-0.6</td>
<td>7</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Maple wood powder</td>
<td>3</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Hexamine (HMTA)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Zinc stearate</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

(Figure 3.1). Specimen dimensions according to the ASTM D638-10 standard
3.5 Characterization of Molding Composites from Liquefied Bark Novolac Resins

3.5.1 Mechanical Test

The tensile strength, strain and Young’s modulus (MOE) of novolac Lab-PF-0.6 and LBPF-C-0.6 molding composites were tested according to the ASTM D638-10 standard with a crosshead speed of 3 mm/min. The mechanical properties obtained from the test were discussed in the result section.

3.5.2 Water Soaking Test

For each molding formula (i.e. Lab-PF-0.6 and LBPF-C-0.6 composite specimens with resin to filler ratio of 7:3, 5:5 and 3:7), three molding composite samples were selected after the mechanical test and used for the water-soaking test. There were total six sampling points marked for each composite specimen, as shown in Figure 3.2, in order to measure the thickness swelling and water absorption. The initial thickness and weight of each composite specimen were measured before the test. All the test composite specimens were then immersed in the distilled water under room temperature and 50% RH.

The test specimens were regularly removed from the water bath every 24 hours and dried with paper towel to remove excess water on the surface of the specimen. The thickness and weight of each specimen was then measured, using caliper and scale accordingly, and recorded to determine the thickness swelling and change in weight after absorbing water for total 336 hours (14 days). The amount of water absorption ($W_t$) and thickness swelling (TS) were calculated using following equations:

Water Absorption: $W_t (%) = \frac{W_t - W_o}{W_o} \times 100$

Where $W_t$ is the weight of test specimen measured at certain water soaking time $t$ and $W_o$ is the initial weight of test specimen before the test.

Thickness Swelling: $TS (%) = \frac{T_t - T_o}{T_o} \times 100$

Where $T_t$ is the thickness of test specimen measured at certain water soaking time $t$ and $T_o$ is the initial thickness of test specimen before the test.
3.5.3 Scanning Electron Microscopy (SEM)

The morphology of the molding composites including the fiber-matrix interaction was observed by the scanning electron microscopy. JEOL model JSM-6610 LV type of scanning electron microscope was used. The fractured molding composite samples were attached to metal stubs and were coated with a thin layer of gold using a SC7620 model sputter coater manufactured by Qoroum Technology.

3.5.4 Thermal Stability

Thermal gravimetric analyzer (TGA-Q500, TA Instruments, USA) was used for analyzing the thermal stability of the molding composites. An approximate 10 mg of grounded composite testing sample molded with lab-made novolac resins and liquefied bark PF novolac resins was loaded in a platinum pan and heated in the combustion chamber from room temperature to 800 °C at the rate of 10 °C/min under the nitrogen atmosphere.
Chapter 4

Bark Phenol Liquefaction Reaction

4.1 Introduction

This chapter investigated the results from mountain pine beetle (MPB, *Dendroctonus ponderosae* Hopkins) infested lodgepole pine (*Pinus contorta* Dougl.) bark phenol liquefaction reaction with different acid catalysts. Mountain pine beetle infested lodgepole pine barks were liquefied in phenol at a set temperature of 150°C for 120 min with a phenol to bark weight ratio of 3:1. The bark phenol liquefaction was conducted under the acid catalysis of either sulfuric acid or hydrochloric acid, which the resulting phenol liquefied bark was denoted as LB-S and LB-C respectively. The catalyst loading was 3% based on the phenol weight. The impacts of different acid catalysts on the liquefaction yield, free phenol content, properties, compositions and structure of the liquefied bark fraction, chemical compositions of the unliquefied bark residues were discussed to systematically understand the effectiveness of bark phenol liquefaction under acid catalysis as a conversion method for obtaining adequate partial phenol substitute from the MPB infested lodgepole pine barks.

A version of this chapter was published in the Macromolecular Reaction Engineering Journal (2013).

4.2 Results and Discussion

4.2.1 Liquefaction Yield and Liquefied Bark Characteristics

The residue ratio, liquefaction yield and free phenol content of bark liquefaction are presented in Table 4.1. It is shown that H$_2$SO$_4$ catalyzed bark phenol liquefaction (LB-S) had lower unliquefied bark residues and a lower free phenol content in the liquefied bark fraction than the HCl catalyzed bark phenol liquefaction (LB-C). The LB-S also had a higher bark phenol liquefaction yield and higher molecular weight in comparison to the LB-C.
According to literatures [46, 3, 36, 47, 14 -16], mineral acids, such as H$_2$SO$_4$ and HCl, were reported to be effective catalysts for the biomass phenol liquefaction. According to our study, it was found that bark could be more effectively liquefied under H$_2$SO$_4$ catalysis resulting in a higher liquefaction yield and reduced free phenol content in the liquefied bark fraction, in comparison to the HCl catalyzed bark liquefaction. Similar results have been observed for wood phenol liquefaction [46, 14 – 16], where H$_2$SO$_4$ catalyzed wood phenol liquefaction was found to have less amount of wood residues and higher reacted phenol fractions in the degraded wood components than HCl catalyzed wood phenol liquefaction.

| Table 4.1. Residue ratios, yield and free phenol content of bark liquefaction |
|-------------------------------------------------|-----------------|-----------------|
|                                                   | H$_2$SO$_4$ catalyzed bark liquefaction | HCl catalyzed bark liquefaction |
| Unliquefied bark residues (%)                    | 11.9 (4.1)       | 30.2 (3.1)       |
| Yield of bark liquefaction (%)                   | 88.1 (4.1)       | 69.8 (3.1)       |
| Free phenol content in the liquefied bark fraction (%) | 45.6             | 53.8             |
| Mw (Da)                                          | 1092.9           | 911.3            |
| Mn (Da)                                          | 529.2            | 322.5            |

*Values in bracket are standard deviations.

According to the previous study from our research group [48], phenolated lignin products, such as phenylcoumaranes, benzocyclobutanes, triphenylethanes, diphenylmethanes, and guaiacol structures and fragments, and phenolated cellulose products, such as tri(4-hydroxylphenyl)methane and 1,1,2-tri(4-hydroxylphenyl)ethane, were found in the liquefied bark. During the liquefaction, the bark components first went through degradation and chemical bond formation/cleavage. The degraded products were then reacted with phenol to form phenolated bark components through additional reactions.
The FTIR spectra of the H$_2$SO$_4$ catalyzed liquefied bark (LB-S) and HCl catalyzed liquefied bark (LB-C) was presented in the Figure 4.1. The major peak assignments were summarized in Table 4.2 based on the published literatures [35, 49 - 51]. The strong and broad band at around 3400 cm$^{-1}$ indicated the O-H absorbance from phenolated carbohydrates or lignin in the liquefied bark or free phenol. The peak at 2918 cm$^{-1}$ was assigned to the CH$_2$ group. The C=O stretching in conjugated ketone groups, ester, or carboxylic groups mostly from carbohydrates such as hemicellulose was indicated by the peak at 1695 cm$^{-1}$. Peaks at 1593 and 1506 cm$^{-1}$ were attributed to aromatic skeletal vibration. The peak at 1340 cm$^{-1}$ was caused by the asymmetrical deformation of C-H. The small peak at 1431 cm$^{-1}$ was associated with the aromatic skeletal vibration combined with C-H in-plane deformation. The S-ring and G-ring in lignin and phenolic hydroxyl group was represented by the peak at 1340 cm$^{-1}$. The intense peak at 1215 cm$^{-1}$ indicated the C=C, C-O and C=O absorbance, proving the appearance of the phenol-lignin complex in the liquefied bark component, which matched with the findings from earlier studies. [48, 51] Peaks at 1168 and 1140 cm$^{-1}$ were associated with C-H in-plane deformation in guaiacyl, and C-H in-plane deformation in syringyl with secondary alcohols and C=O stretch, accordingly. Moreover, peaks at 1095, 1072, and 1028 cm$^{-1}$ were responding to C-O deformation in secondary alcohols and aliphatic esters, and C-O deformation in primary alcohols along with C-H in-plane deformation in guaiacyl, accordingly.

![FTIR spectra of liquefied barks](image-url)

**Figure 4.1.** FTIR spectra of liquefied barks.
Peaks at 1460 and 1431 cm\(^{-1}\) were more intense in the FTIR spectrum of LB-C than in the spectrum of LB-S, which might be attributed to the higher free phenol content and less phenolated structures in the LB-C than LB-S. In addition, stronger peaks at 1095 and 1072 cm\(^{-1}\) were observed in the LB-C spectrum, which indicated that there were more primary alcohols, secondary alcohols, and aliphatic esters C-O bond deformations occurred in the LB-C. This might due to the fact that there were more unliquefied lignin and less phenolics in the LB-C in comparison to the phenolated content in LB-S.

Table 4.2. Peak assignment of the FTIR spectra of liquefied bark and residues from bark liquefaction. [35, 49 – 51]

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Peak assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400 – 3500</td>
<td>- OH stretch</td>
</tr>
<tr>
<td>2918</td>
<td>C-H stretch in CH(_3) or CH(_2) groups</td>
</tr>
<tr>
<td>1695</td>
<td>C=O stretching in conjugated ketone groups, ester, or carboxylic groups</td>
</tr>
<tr>
<td>1593, 1506</td>
<td>Aromatic skeletal vibration</td>
</tr>
<tr>
<td>1460</td>
<td>C-H asymmetrical deformation</td>
</tr>
<tr>
<td>1431</td>
<td>Aromatic skeletal vibration combined with C-H in-plane deformation</td>
</tr>
<tr>
<td>1340</td>
<td>S-ring and G-ring in lignin and phenolic hydroxyl group</td>
</tr>
<tr>
<td>1326</td>
<td>Condensed G-ring in lignin</td>
</tr>
<tr>
<td>1215</td>
<td>C-C, C-O and C=O stretch</td>
</tr>
<tr>
<td>1168</td>
<td>C-H in-plane deformation in guaiacyl</td>
</tr>
<tr>
<td>1140</td>
<td>C-H in-plane deformation in syringyl plus secondary alcohols and C=O stretch</td>
</tr>
<tr>
<td>1095, 1072</td>
<td>C-O deformation in secondary alcohols and aliphatic esters</td>
</tr>
<tr>
<td>1028, 1024, 1012</td>
<td>C-O deformation in primary alcohols plus C-H in-plane deformation in guaiacyl</td>
</tr>
</tbody>
</table>
4.2.2 Unliquefied Residues from Bark Liquefaction

The chemical compositions of residues from bark liquefaction is presented in Table 4.3. It was reported that HCl catalyzed liquefied bark residues contained significant higher lignin content than the residues from H$_2$SO$_4$ catalyzed bark liquefaction, which indicated that H$_2$SO$_4$ catalyst liquefied the lignin component in bark more effectively than the HCl catalyst in the bark-phenol liquefaction. According to previous studies [14-16, 36, 46–47, 51], lignin was found as the most reactive components with the high tendency to go through secondary condensation reactions in phenol liquefaction; whereas, cellulose was found as the least reactive components in phenol liquefaction. However, phenol reacted with degraded lignin during the liquefaction process to form a new insoluble intermediate that would stay in the residue, which would affect the Klason lignin determination [51]. Similar amount of holocellulose, alpha-cellulose, and hemicellulose content were found in the residues from both H$_2$SO$_4$ catalyzed and HCl catalyzed bark phenol liquefaction, which indicated that both H$_2$SO$_4$ and HCl catalyst could effectively liquefy the carbohydrates in bark during the phenol liquefaction. Overall, H$_2$SO$_4$ catalyst is more efficient in bark phenol liquefaction, which results in higher liquefaction yield and lower residue content, than HCl catalyst.

Table 4.3. Chemical compositions of residues from bark liquefaction.

<table>
<thead>
<tr>
<th></th>
<th>Hemicellulose (%)</th>
<th>Alpha-cellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residues from H$_2$SO$_4$ catalyzed bark liquefaction</td>
<td>56.0 (2.0)</td>
<td>23.6 (0.1)</td>
<td>39.5 (5.8)</td>
</tr>
<tr>
<td>Residues from HCl catalyzed bark liquefaction</td>
<td>53.6 (1.1)</td>
<td>25.5 (1.5)</td>
<td>55.1 (2.7)</td>
</tr>
</tbody>
</table>

Values in bracket are standard deviations.
Figure 4.2. FTIR spectra of residues from bark phenol liquefaction

The FTIR spectra of residues from acid-catalyzed bark phenol liquefaction are presented in Figure 4.2. The peak assignments were summarized in Table 4.2 according to the published literatures. [49, 51 – 52] The broad peak between 3400 and 3500 cm\(^{-1}\) was the O-H stretching. The peak at 2918 cm\(^{-1}\) was due to the C-H absorbance in methyl and methylene groups. Peaks at 1595 and 1504 cm\(^{-1}\) were attributed to the aromatic skeletal vibration. The peak at 1460 cm\(^{-1}\) was caused by the asymmetrical deformation of C-H stretching. The peak at 1431 cm\(^{-1}\) was due to the aromatic skeletal vibration combined with C-H in-plane deformation. Peaks at 1095, 1024, and 1012 cm\(^{-1}\) indicated the C-O deformation in secondary alcohols and aliphatic esters, the C-O deformation in primary alcohols, and the C-H in-plane deformation in guaiacyl, accordingly. The peak at 1695 cm\(^{-1}\) was more intense in the residues from H\(_2\)SO\(_4\) catalyzed liquefied bark than in the residues from HCl catalyzed liquefied bark. This peak was associated with the carbonyl bond in conjugated ketone groups, ester, or carboxylic groups, which mainly from carbohydrates in hemicellulose or oxidative products of cellulose.
By comparing the spectrum of the residues from H$_2$SO$_4$ catalyzed bark phenol liquefaction and the residues from HCl catalyzed bark phenol liquefaction, a new peak appeared at 1326 cm$^{-1}$ in the spectrum of the residues from HCl catalyzed bark liquefaction. According to previous studies [51–52], this peak was responding to the condensed G-ring in lignin, which might be attributed to a higher amount of lignin by-product from the re-condensation reaction during the liquefaction or a higher amount of unliquefied lignin in the HCl catalyzed liquefied bark residues. The peak at 1215 cm$^{-1}$ was stronger in the spectrum of residues from LB-C than in the residues from LB-S. This peak was assigned to C-C, C-O and C=O stretch meaning that there was more phenol-lignin complex in the residues from LB-C in comparison to the residues from LB-S, which agreed with our finding that residues from LB-C contained higher lignin content. Moreover, the intensity of the peak at 1168 cm$^{-1}$ caused by the C-H in-plane deformation in guaiacyl was stronger in the residues from LB-C than in the residues from LB-S, which was consistent with the fact that H$_2$SO$_4$ catalyst is more efficient in liquefying lignin than HCl catalyst.

4.3 Conclusion

The acid-catalyzed bark phenol liquefaction was an effective method to convert mountain pine beetle (MPB) infested lodgepole pine bark into suitable phenol substitute. The change in catalyst type significantly affected the liquefaction yield, free phenol content, properties and characteristics of the resulting liquefied bark component and the unliquefied residues. It was found that both sulfuric acid and hydrochloric acid could effectively catalyze the bark-phenol liquefaction to obtain adequate phenol substitute with the maximum yield of 88.1% and 69.8% respectively. Sulfuric acid catalyst was found to be more effective in bark phenol liquefaction, which resulted in a higher liquefaction yield and a lower free phenol content in the liquefied bark fraction as well as lower residue content in comparison to the hydrochloric catalyzed bark phenol liquefaction. Moreover, it was reported that HCl catalyzed liquefied bark residues contained significant higher lignin content than the residues of H$_2$SO$_4$ catalyzed liquefied bark, which further proved that H$_2$SO$_4$ catalyst liquefied the lignin component in bark more effectively than the HCl catalyst in the bark-phenol liquefaction.
Chapter 5
Liquefied Bark Novolac Resins

5.1 Introduction

In this chapter, the liquefied bark components were directly used as partial phenol substitute to react with formaldehyde at 85°C under acidic condition for 120 min to synthesize the bio-based PF novolac resins. The liquefied bark novolac PF resin with sulfuric acid catalyzed liquefied bark component was denoted as liquefied bark novolac PF resin S (LBPF-S). The liquefied bark novolac PF resin derived from the hydrochloric acid catalyzed liquefied bark component was denoted as liquefied bark novolac PF resin C (LBPF-C). These synthesized liquefied bark PF novolac resins were tested to compare with a lab-made control novolac resins, which does not contain liquefied bark components, in order to investigate resin properties, curing behavior and thermal stability. The characterization results of LBPF-S and LBPF-C resins will be discussed in the following sections.

A version of this chapter was published in the Macromolecular Reaction Engineering Journal (2013).

5.2 Results and Discussions

5.2.1 Resin Properties

The solids content of lab-made novolac phenol formaldehyde resins (Lab PF) were reported in Table 5.1. It was found that the solids content of lab-made novolac resins increased as the formaldehyde to phenol molar ratio increased in resin formulations, where Lab PF with 0.8 formaldehyde to phenol ratio had the highest solids content while Lab PF 0.4 had the least solids content. The liquefied bark novolac phenol formaldehyde resins synthesized using both H\textsubscript{2}SO\textsubscript{4} and HCl catalyzed liquefied bark were in the solid forms after drying; therefore, the solids content were not tested for LBPF-S 0.4, LBPF-S 0.6, LBPF-S 0.8, LBPF-C 0.4, LBPF-C 0.6, and LBPF-C 0.8.
The molecular weight of each Lab PF resins and LBPF resins were presented in Table 5.2. It was reported that the molecular weight of synthesized resins increased as the formaldehyde to phenol molar ratio increased in the resin formulation. Overall, the lab-made control resins had a lower molecular weight than the liquefied bark novolac phenol formaldehyde resins at all formaldehyde to phenol molar ratios or to liquefied bark weight ratios. LBPF-S resins had a higher molecular weight than LBPF-C resins at all formaldehyde to liquefied bark weight ratios, which might due to the higher amount of phenolated components in the LBPF-S resins.

Table 5.1. Solids content in the Lab-made phenol formaldehyde resins.

<table>
<thead>
<tr>
<th>Resins</th>
<th>Solids Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab PF 0.4</td>
<td>56.96</td>
</tr>
<tr>
<td>Lab PF 0.6</td>
<td>72.50</td>
</tr>
<tr>
<td>Lab PF 0.8</td>
<td>88.68</td>
</tr>
</tbody>
</table>

Table 5.2. Molecular weight of the phenol formaldehyde resins.

<table>
<thead>
<tr>
<th>Resins</th>
<th>$M_W$</th>
<th>$M_n$</th>
<th>$M_W/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab PF 0.4</td>
<td>721.13</td>
<td>427.59</td>
<td>1.69</td>
</tr>
<tr>
<td>Lab PF 0.6</td>
<td>1048.06</td>
<td>524.24</td>
<td>2.00</td>
</tr>
<tr>
<td>Lab PF 0.8</td>
<td>1221.34</td>
<td>376.77</td>
<td>3.24</td>
</tr>
<tr>
<td>LBPF-S 0.4</td>
<td>1886.6</td>
<td>870.87</td>
<td>2.17</td>
</tr>
<tr>
<td>LBPF-S 0.6</td>
<td>2381.6</td>
<td>908.83</td>
<td>2.62</td>
</tr>
<tr>
<td>LBPF-S 0.8</td>
<td>2562.4</td>
<td>932.25</td>
<td>2.75</td>
</tr>
<tr>
<td>LBPF-C 0.4</td>
<td>1381.24</td>
<td>386.01</td>
<td>3.58</td>
</tr>
<tr>
<td>LBPF-C 0.6</td>
<td>1617.74</td>
<td>590.31</td>
<td>2.74</td>
</tr>
<tr>
<td>LBPF-C 0.8</td>
<td>1986.21</td>
<td>439.32</td>
<td>4.52</td>
</tr>
</tbody>
</table>

5.2.2 DSC Analysis of the Resins

Hexamethylenetetramine (HMTA) was used as curing agent for both lab-made control PF resins (Lab PF) and liquefied bark novolac PF resins (LBPF) in our experiments.
According to previous studies [53 – 60], HMTA decomposed and reacted with phenolic rings in the resin during the initial stage of the curing process to form several intermediate products such as benzylamine and benzoazine. These intermediate products would further go through condensation reaction and eventually formed macromolecules, which were the cured resin (Figure 5.1).

![Curing reaction of novolac PF resin with curing agent HMTA.](image)

**Figure 5.1.** Curing reaction of novolac PF resin with curing agent HMTA. [53 – 60]

Dynamic DSC curves of the lab-made novolac resins are presented in Figure 5.2. There were two exothermic peaks appeared on the dynamic DSC curves for the lab-made control novolac resins with formaldehyde to phenol ratio of 0.6 (Lab PF 0.6). Same trend was observed for the other two lab-made control novolac resins with formaldehyde to phenol ratio of 0.4 and 0.8 (Lab PF 0.4 and Lab PF 0.8). The first peak could be
associated with the addition reactions between the novolac resin and the curing agent, HMTA, and the second peak could be due to the condensation reactions as mentioned before. [61 – 64]

![Dynamic DSC curves of lab-made control novolac resin (Lab PF 0.6).](image)

**Figure 5.2.** Dynamic DSC curves of lab-made control novolac resin (Lab PF 0.6).

<table>
<thead>
<tr>
<th>Heating rate [°C/min]</th>
<th>Lab PF 0.4</th>
<th></th>
<th>Lab PF 0.6</th>
<th></th>
<th>Lab PF 0.8</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset Temp.</td>
<td>Peak Temp. 1</td>
<td>Peak Temp. 2</td>
<td>Onset Temp.</td>
<td>Peak Temp. 1</td>
<td>Peak Temp. 2</td>
</tr>
<tr>
<td>0</td>
<td>108.7</td>
<td>121.8</td>
<td>175.1</td>
<td>108.7</td>
<td>121.3</td>
<td>175.4</td>
</tr>
<tr>
<td>5</td>
<td>113.8</td>
<td>129.7</td>
<td>186.5</td>
<td>114.0</td>
<td>128.6</td>
<td>186.0</td>
</tr>
<tr>
<td>10</td>
<td>127.6</td>
<td>142.1</td>
<td>202.1</td>
<td>123.1</td>
<td>141.3</td>
<td>202.2</td>
</tr>
<tr>
<td>15</td>
<td>135.2</td>
<td>151.1</td>
<td>215.1</td>
<td>124.2</td>
<td>149.0</td>
<td>214.7</td>
</tr>
<tr>
<td>20</td>
<td>137.8</td>
<td>157.9</td>
<td>225.0</td>
<td>133.7</td>
<td>156.0</td>
<td>223.5</td>
</tr>
</tbody>
</table>

**Table 5.3.** Curing temperatures of lab-made novolac resins.
The onset and peak temperatures for lab-made control novolac resins were summarized in Table 5.3. The cure reaction happened only when the temperature is higher than the onset temperature, while the peak temperatures are the temperatures where the highest cure rate was observed. As the heating rate increased, both the onset and peak temperature shifted towards to higher temperatures. For a better comparison between resins with different formaldehyde to phenol ratios, all the onset and peak temperatures were extrapolated to the heating rate of zero because the actual cure temperatures should be independent of the heating rate. [17 – 18, 62 – 64] The extrapolated onset and two peak temperatures, with the heating rate equal to zero, were 108.7, 121.8, and 175.1 °C respectively for Lab PF 0.4, 108.7, 121.3, and 175.4 °C respectively for Lab PF 0.6, and 108.2, 121.6, and 176.9 °C respectively for Lab PF 0.8. There were no significant differences in the onset and peak temperatures for the lab-made control novolac resins with different formaldehyde to phenol molar ratios of 0.4, 0.6 and 0.8. The formaldehyde to phenol molar ratios in the synthesis of novolac phenol formaldehyde resins is less than one; therefore, the resulting resins acquire a linear structure due to the insufficient of formaldehyde during the resin synthesis. The curing agents are usually required to cure the novolac resins in order to attain a final resin product with a three-dimensional crosslinking structure. Thus, for lab-made control novolac PF resins, different formaldehyde to phenol molar rations of 0.4, 0.6 and 0.8 did not affect the curing activity of the resulting resins.

According to the earlier studies from our research group on the resol PF resins with bark components [17 – 18], it was found that the addition of either liquefied bark or bark extractives in the formulation of resol PF resins affected the curing behavior of the resins. Thus, it was expected that the liquefied bark components in the novolac PF resins would also affect the curing behavior of the resins.

The dynamic DSC curves of HCl acid-catalyzed liquefied bark novolac resins (LBPF-C 0.6) and H_{2}SO_{4} acid-catalyzed liquefied bark novolac resins (LBPF-S 0.6) are presented in Figure 5.3 and 5.4 respectively. Two major exothermic peaks were observed in the dynamic DSC curve of LBPF-C 0.6, which is similar to the reference dynamic DSC curve of Lab-PF 0.6; however, only one exothermic peak was observed in the dynamic
DSC curve of LBPF-S 0.6. The dynamic DSC curves of LBPF-C 0.4, LBPF-C 0.8, LBPF-S 0.4, and LBPF-S 0.8 followed the same trend as the curves of LBPF-C 0.6 and LBPF-S 0.6. Moreover, the small exothermic peak in the LBPF-C 0.6 curves at around 85-90 °C might be associated with the methylolation reactions of free formaldehyde to phenol. [65]

The differences in the curing behavior between LBPF-C and LBPF-S resins could be due to the structural or compositional difference of the HCl acid-catalyzed phenol liquefied bark (LB-C) and H$_2$SO$_4$ acid-catalyzed phenol liquefied bark (LB-S). The LB-S contained more degraded bark component and phenolated compounds than LB-C, which might have more reactive sites to react with formaldehyde and the curing agent for the polymerization attaining a more cross-linking structure in the resulting resins LBPF-S. However, the detailed differences between the structure of LB-S and the structure of LB-C are still under investigation.

![Figure 5.3. Dynamic DSC curves of HCl acid-catalyzed liquefied bark novolac PF resins (LBPF-C 0.6).](image)
Figure 5.4. Dynamic DSC curves of H$_2$SO$_4$ acid-catalyzed liquefied bark novolac PF resins (LBPF-S 0.6).

The onset and peak temperatures of H$_2$SO$_4$ acid-catalyzed liquefied bark novolac PF resins (LBPF-S) and HCl acid-catalyzed liquefied bark novolac PF resins (LBPF-C) are shown in Table 5.4 and 5.5, respectively. For LBPF-S resins, the extrapolated onset and peak temperatures with the heating rate equal to zero were 105.8 and 120.3 °C for LBPF-S 0.4, 112.7 and 136.2 °C for LBPF-S 0.6, and 129.6 and 141.7 °C for LBPF-S 0.8. For LBPF-C resins, the extrapolated onset and two peak temperatures with zero heating rate were 92.8, 118.1 and 177.5 °C respectively for LBPF-C 0.4, 106.5, 125.9 and 205.6 °C respectively for LBPF-C 0.6 and 115.9, 131.4 and 207.2 °C respectively for LBPF-C 0.8. For both LBPF-S and LBPF-C resins, the onset and peak temperatures increased as the formaldehyde to liquefied bark weight ratio increased in the resin formulation. This indicated that the higher amount of formaldehyde usage in resin formulation reduced the curing activity of the resulting liquefied bark novolac PF resins. LBPF-S 0.4 and LBPF-C 0.4 had lower onset and peak temperature than the Lab PF 0.4, meaning that the curing activity increased in the novolac PF resins with liquefied bark component at relatively low formaldehyde to liquefied bark weight ratio. LBPF-S 0.6, LBPF-S 0.8, LBPF-C 0.6 and LBPF-C 0.8 had higher onset and peak temperatures than Lab PF 0.6 and Lab PF 0.8. This indicated that higher amount of formaldehyde usage in the resin synthesis would lower the curing activity in the resulting novolac resins with liquefied bark components. Therefore, the formaldehyde to liquefied bark weight ratios had a significant effect on the
curing activity of liquefied bark novolac PF resins for both LBPF-S and LBPF-C resins. Moreover, H$_2$SO$_4$ acid-catalyzed liquefied bark novolac PF resins had higher onset and peak temperatures than the HCl acid-catalyzed liquefied bark novolac PF resins at all selected formaldehyde to liquefied bark weight ratios. This could be associated with the fact that H$_2$SO$_4$ acid-catalyzed phenol liquefied bark had a higher molecular weight and more phenolated structures than the HCl acid-catalyzed phenol liquefied bark, which might caused the relatively lower curing activity in LBPF-S resins.

Table 5.4. Curing temperatures of H$_2$SO$_4$ acid-catalyzed liquefied bark novolac resins (LBPF-S).

<table>
<thead>
<tr>
<th>Heating rate [°C/min]</th>
<th>LBPF-S 0.4</th>
<th></th>
<th>LBPF-S 0.6</th>
<th></th>
<th>LBPF-S 0.8</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>105.8</td>
<td>120.3</td>
<td>112.7</td>
<td>136.2</td>
<td>129.6</td>
<td>141.7</td>
</tr>
<tr>
<td>5</td>
<td>111.5</td>
<td>129.1</td>
<td>120.1</td>
<td>143.7</td>
<td>135.7</td>
<td>150.1</td>
</tr>
<tr>
<td>10</td>
<td>117.2</td>
<td>137.3</td>
<td>126.6</td>
<td>152.3</td>
<td>143.7</td>
<td>160.1</td>
</tr>
<tr>
<td>15</td>
<td>125.1</td>
<td>148.1</td>
<td>133.5</td>
<td>158.9</td>
<td>152.1</td>
<td>170.1</td>
</tr>
<tr>
<td>20</td>
<td>128.1</td>
<td>154.7</td>
<td>141.4</td>
<td>167.3</td>
<td>155.8</td>
<td>176.7</td>
</tr>
</tbody>
</table>

Table 5.5. Curing temperatures of HCl acid-catalyzed liquefied bark novolac resins (LBPF-C).

<table>
<thead>
<tr>
<th>Heating rate [°C/min]</th>
<th>Lab PF 0.4</th>
<th></th>
<th>Lab PF 0.6</th>
<th></th>
<th>Lab PF 0.8</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset Temp.</td>
<td>Peak Temp. 1</td>
<td>Peak Temp. 2</td>
<td>Onset Temp.</td>
<td>Peak Temp. 1</td>
<td>Peak Temp. 2</td>
</tr>
<tr>
<td>0</td>
<td>92.8</td>
<td>118.1</td>
<td>177.5</td>
<td>106.5</td>
<td>125.9</td>
<td>205.6</td>
</tr>
<tr>
<td>5</td>
<td>102.3</td>
<td>125.3</td>
<td>188.3</td>
<td>113.5</td>
<td>132.1</td>
<td>212.1</td>
</tr>
<tr>
<td>10</td>
<td>107.3</td>
<td>137.1</td>
<td>204.1</td>
<td>119.3</td>
<td>141.4</td>
<td>223.2</td>
</tr>
<tr>
<td>15</td>
<td>119.3</td>
<td>145.6</td>
<td>216.4</td>
<td>127.4</td>
<td>149.3</td>
<td>230.7</td>
</tr>
<tr>
<td>20</td>
<td>126.3</td>
<td>151.6</td>
<td>225.5</td>
<td>133.3</td>
<td>155.5</td>
<td>236.2</td>
</tr>
</tbody>
</table>
5.2.3 Activation Energy and Pre-exponential Factors

The curing activation energy and pre-exponential factor of all the synthesized resins were listed in Table 5.6. As formaldehyde to phenol molar ratios or formaldehyde to liquefied bark weight ratios increased in resin synthesis, the curing activation energy increased for both lab-made control novolac resins and liquefied bark novolac resins. Higher curing activation energy indicates that the resin required higher thermal energy to cure. It is understandable since higher amount of formaldehyde used in the resin formulation will increase the cross-linking structures in the synthesized resin, which reduce molecular mobility in the synthesized resin and could be harder for the resin to react with the crosslinking agent, HMTA, to form a further highly cross-linking structures during the curing process; thus, the curing activation energy would increase. For the resins formulated with the same formaldehyde to phenol molar ratios or formaldehyde to liquefied bark weight ratios, both H$_2$SO$_4$ acid-catalyzed liquefied bark novolac resins and HCl acid-catalyzed liquefied bark novolac resins had higher curing activation energy than the lab-made control novolac resins. This could be due to the fact that novolac resins synthesized with acid-catalyzed liquefied bark components contained significant amounts of liquefied bark components with larger molecular size and also LBPF-S and LBPF-C resins had higher molecular weight than lab-made control novolac resins, which reduced the mobility of resin molecules and thus required higher curing activation energy during the curing process. It was consistent with our previous studies on the liquefied bark resol PF resins [17], the large degraded bark components in the liquefied bark fraction lower the mobility of the resin molecules to form cross-links during the curing process, which increased the resin curing activation energy. Moreover, the lab-made control novolac resins were in liquid form after synthesis reaction, whereas, the liquefied bark novolac resins acquired a solid form after the resin synthesis. This agreed with our results since solids are generally harder to react with curing agent and to be cured during the curing process.

It was observed that the pre-exponential factors of both lab-made control novolac resins and liquefied bark novolac resins increased with the increasing formaldehyde to phenol molar ratios and formaldehyde to liquefied bark weigh ratios during resin synthesis. Also,
higher pre-exponential factors were found in the liquefied bark novolac resins in comparison to the lab-made control novolac resins at the same formaldehyde to liquefied bark weight ratios or formaldehyde to phenol molar ratios in resin formulations. Higher pre-exponential factor means a faster curing rate of the resulting resins. The higher pre-exponential factor found in the liquefied bark novolac resins might be associated with the reactive sites on the bark components and the self-condensation capability of the liquefied bark components.

**Table 5.6.** Curing characteristics of all the synthesized resins

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab PF 0.4</td>
<td>121.8</td>
<td>175.1</td>
<td>63.82</td>
<td>60.36</td>
<td>4.64×10⁷</td>
<td>1.31×10⁶</td>
</tr>
<tr>
<td>Lab PF 0.6</td>
<td>121.3</td>
<td>175.4</td>
<td>66.27</td>
<td>61.88</td>
<td>1.05×10⁸</td>
<td>2.01×10⁶</td>
</tr>
<tr>
<td>Lab PF 0.8</td>
<td>121.6</td>
<td>176.9</td>
<td>69.92</td>
<td>63.22</td>
<td>3.33×10⁸</td>
<td>2.76×10⁶</td>
</tr>
<tr>
<td>LBPF-C 0.4</td>
<td>118.1</td>
<td>177.5</td>
<td>67.09</td>
<td>63.14</td>
<td>1.65×10⁸</td>
<td>2.57×10⁶</td>
</tr>
<tr>
<td>LBPF-C 0.6</td>
<td>125.9</td>
<td>205.6</td>
<td>81.36</td>
<td>109.64</td>
<td>9.45×10⁹</td>
<td>1.85×10¹¹</td>
</tr>
<tr>
<td>LBPF-C 0.8</td>
<td>131.4</td>
<td>207.2</td>
<td>84.91</td>
<td>111.0</td>
<td>1.98×10¹⁰</td>
<td>2.34×10¹¹</td>
</tr>
<tr>
<td>LBPF-S 0.4</td>
<td>120.3</td>
<td>N/A</td>
<td>67.4</td>
<td>N/A</td>
<td>1.60×10⁸</td>
<td>N/A</td>
</tr>
<tr>
<td>LBPF-S 0.6</td>
<td>136.2</td>
<td>N/A</td>
<td>79.98</td>
<td>N/A</td>
<td>7.81×10⁹</td>
<td>N/A</td>
</tr>
<tr>
<td>LBPF-S 0.8</td>
<td>141.7</td>
<td>N/A</td>
<td>89.97</td>
<td>N/A</td>
<td>1.09×10¹¹</td>
<td>N/A</td>
</tr>
</tbody>
</table>

N/A: not applicable.

Overall, our results were very similar to the curing characteristics of liquefied bark resol PF resins [17], where the lab-made control resins without the liquefied bark components and resins with higher formaldehyde usage in resin formulation were more thermodynamically favorable to cure than the resins with liquefied bark components according to the required curing energy. Additionally, the liquefied bark novolac resins or resins synthesized with higher amount of formaldehyde usage had a faster curing reaction rate with the sufficient thermal energy available.
5.2.4 Isothermal Curing Behavior of the Resins

The resin conversion rate versus the degree of conversion obtained from the isothermal DSC was presented in Figure 5.5 – 5.7. Both n-th order and autocatalytic cure mechanisms were observed in the novolac resin curing process. The autocatalytic cure mechanism was found to be dominant at higher cure temperatures. This finding agreed with the previous studies on the liquefied bark resol PF resins synthesized from MPB infested lodgepole pine [17]. According to the isothermal DSC curves, lab-made control novolac resins had faster conversion rate than liquefied bark novolac resins. This might due to the fact that samples were heated to a designated temperature in a very short time while the autocatalytic cure reaction for liquefied bark novolac resins and the auto-condensation reaction of the liquefied bark may start at temperatures below the designated temperature due to the degraded bark component in the resin formulation, which the conversion rate at 0% conversion on the graph might not be the peak conversion rate during the entire curing process. The dynamic DSC curves represented a completed spectrum for the resin curing activity as the temperature were gradually increased from the room temperature to the designated temperature during the curing process and the full temperature profile was investigated. During the curing process of liquefied bark novolac resins, auto-condensation reactions in the liquefied bark component happened, which might have contributed to the faster curing rate in comparison to the lab-made control resins. However, the auto-condensation reactions of the liquefied bark component might be eliminated from the isothermal DSC curves at the higher isothermal curing temperature if the designated isothermal temperature was too high and past the auto-condensation reactions temperature. Thus, the conversion rate from the isothermal DSC curves might not represent the true conversion rate of the entire curing process.
Figure 5.5. Conversion rate as a function of degree of conversion at various isothermal temperatures for the lab-made control novolac resin (Lab PF 0.6).

Figure 5.6. Conversion rate as a function of the degree of conversion at various isothermal temperatures for the H$_2$SO$_4$ acid-catalyzed liquefied bark novolac PF resin (LBPF-S 0.6).
Conversion rates of resins as a function of time at different isothermal cure temperature were shown in **Figure 5.8 – 5.10**. The resin cure reaction reached the same level of conversion in a shorter time at a higher isothermal curing temperature. For example, the HCl catalyzed novolac PF resins (**Figure 5.10**) reached 90% of the conversion after 10 minutes of the cure reaction when the isothermal curing temperature was at 150°C; while it took 27 minutes to reach 90% of the conversion at 110°C. Same trend was observed for Lab PF resins (**Figure 5.8**) and LBPF-S resins (**Figure 5.9**). This result is very important for choosing the appropriate molding temperature and time for our molding composite in order to ensure that the resins are completely cured during the molding process. The shape of the curves changed with different isothermal curing temperatures. The lab-made control novolac resins (**Figure 5.8**) required shorter curing time to reach the same level of conversion than the liquefied bark novolac resins at the isothermal curing temperature of 150°C. At 150°C, Lab PF resins reached 90% of conversion in 5 minutes while both LBPF-S (**Figure 5.9**) and LBPF-C (**Figure 5.10**) resins required approximately 10 minutes to reach 90% of conversion. However, the shape of the curves were similar among these resins when the isothermal curing temperature was below 150°C. The
change of the shape of the curves for liquefied bark novolac resins was different from that for the lab-made control novolac resins might be attributed to the change in the cure mechanism.

**Figure 5.8.** Conversion as a function of cure time at various isothermal temperatures for the lab-made control novolac PF resin (Lab PF 0.6).

**Figure 5.9.** Conversion as a function of cure time at various isothermal temperatures for the H$_2$SO$_4$ acid-catalyzed liquefied bark novolac PF resin (LBPF-S 0.6).
5.2.5 FTIR Spectra of the Resins

The FTIR spectra of uncured and cured lab-made control novolac PF resins, H₂SO₄ acid-catalyzed liquefied bark novolac PF resins and HCl acid-catalyzed liquefied bark novolac PF resins were presented in Figure 5.11 and 5.12, accordingly. The associated peak assignments were summarized in Table 5.7 according to literatures [18, 35, 50].

In all six spectra of uncured and cured lab-made control novolac resins (Lab PF 0.6) and liquefied bark novolac resins (LBPF-S 0.6 and LBPF-C 0.6), the board absorbance from 3100 to 3500 cm⁻¹ was observed, which was due to the O-H group stretching from either phenol or liquefied bark component in the resin formulation. Another significant peak at 2800 – 2900 cm⁻¹ was also found in all six spectra indicating the CH₂ groups. The CH₂ groups in the lab-made control novolac resins were associated with the methylene linkage between phenol and formaldehyde; whereas, the CH₂ groups in the liquefied bark novolac resins could be attributed to the methylene linkage between the phenol or liquefied bark and formaldehyde, or from liquefied bark itself. Before curing, all three resins (Lab PF 0.6, LBPF-S 0.6 and LBPF-C 0.6) had similar intensity at CH₂ absorbance. However, higher intensity was found in the peak of CH₂ groups for both
LBPF-S 0.6 and LBPF-C 0.6 resins after cure in comparison to cured lab-made control resin (Lab PF 0.6). This might be due to the increased cross-linked structures obtained from the curing reaction between the liquefied bark and HMTA or an increased condensed structures from the liquefied bark and formaldehyde or liquefied bark itself during the curing process.

The absorbance at 1693 cm\(^{-1}\) in the spectra of uncured liquefied bark novolac resins (LBPF-S 0.6 and LBPF-C 0.6) were assigned to the carbonyl stretching in conjugated ketone groups, ester, or carboxylic groups that mainly from the degraded bark components in the liquefied bark. This peak was absent in the spectra of cured LBPF-S 0.6 and LBPF-C 0.6 resins, meaning that liquefied bark components reacted with HMTA during the curing process. Peaks at 1591, 1501, 1452, and 1431 cm\(^{-1}\) were associated with the vibration of aromatic rings, and CH\(_3\) and CH\(_2\) asymmetrical stretching. In the spectra of all uncured resins, these four peaks had stronger and clearer absorbance in the spectra of LBPF-S 0.6 and LBPF-C 0.6 resins than in the Lab PF 0.6 spectrum. After the curing process, these four peaks shrunk to a lower intensity for all cured Lab PF 0.6, LBPF-S 0.6 and LBPF-C 0.6 resins.

The peak at 1346 cm\(^{-1}\) indicated the phenol O-H in-plane bending or the S-ring and G-ring in lignin in the liquefied bark was found in the uncured lab-made control novolac resins and two liquefied bark novolac resins, accordingly. This peak disappeared in the cured lab-made control novolac resins, while turned into two weak peaks at 1361 and 1321 cm\(^{-1}\) in the spectra of liquefied bark novolac resins, which were associated with the condensed lignin G-rings from the degraded bark component in the LBPF-S and LBPF-C resins. This finding further indicated that phenol reacted with HMTA in the lab-made control novolac resin and liquefied bark reacted with HMTA or liquefied bark itself in the liquefied bark novolac resins during the resin curing process.

Peaks at 1195, 1166 and 1089 cm\(^{-1}\) were due to the C-O bonding and C-H in-plane deformation. These peaks remained unchanged after the curing process for all the resins. Moreover, the peak at 1014 cm\(^{-1}\) was associated with the aliphatic hydroxyl, which a
stronger absorbance was observed in the spectra of cured liquefied bark novolac resins than in the spectrum of lab-made control novolac resins indicating that it could be from the liquefied bark components.

Table 5.7. Peak assignments of the FTIR spectra of novolac PF resins [18, 35, 50].

<table>
<thead>
<tr>
<th>Wavenumber [cm⁻¹]</th>
<th>Peak Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3100 – 3500</td>
<td>- OH stretch</td>
</tr>
<tr>
<td>2800 – 2900</td>
<td>CH₂ groups</td>
</tr>
<tr>
<td>1693</td>
<td>Carbonyl stretching in conjugated ketone groups, ester, or carboxylic groups</td>
</tr>
<tr>
<td>1591, 1501, 1452, 1431</td>
<td>Vibration of aromatic G-rings in the cured liquefied bark novolac PF resins</td>
</tr>
<tr>
<td>1361, 1326</td>
<td>Condensed lignin G-rings in the cured liquefied bark novolac PF resins</td>
</tr>
<tr>
<td>1346</td>
<td>Phenol O-H in-plane bending or the S-ring and G-ring in lignin</td>
</tr>
<tr>
<td>1195, 1166, 1089</td>
<td>C-O stretching and C- in-plane deformation</td>
</tr>
<tr>
<td>1014</td>
<td>Aliphatic hydroxyl</td>
</tr>
</tbody>
</table>
Figure 5.11. FTIR spectra of uncured resins (Lab PF 0.6, LBPF-S 0.6 and LBPF-C 0.6).

Figure 5.12. FTIR spectra of cured resins (Lab PF 0.6, LBPF-S 0.6 and LBPF-C 0.6).
5.2.6 Thermal Stability of the Resins

Thermal stability of polymers highly depends on their structure and cross-linking density [66]. The thermal stability of all the synthesized resins were tested using the thermal gravimetric analyzer (TGA) and the thermal degradation curves of the uncured lab-made control novolac resins with different formaldehyde to phenol molar ratios were shown in Figure 5.13. According to the TGA curves, the retained weight of the uncured lab-made control novolac resins increased as the formaldehyde to phenol molar ratio increased in the resin synthesis, meaning better thermal stability in the resins synthesized with higher formaldehyde usage. Same trend was found in the TGA curves of uncured liquefied bark novolac resins. For the uncured lab-made control resin with the least formaldehyde to phenol molar ratio (Lab PF 0.4), a significant weight loss started at around 200°C; however, the major weight loss happened at around 350°C for the uncured lab-made control resins with the 0.8 formaldehyde to phenol molar ratio. Resins with higher amount of formaldehyde usage were more thermally stable at lower temperature and also had higher retained weight at the end of experiment. This is understandable since higher formaldehyde usage in the resin formulation would result in a higher molecular weight and a higher cross-linked structure in the resulting resins, which will improve the thermal stability of the resulting resin.

![Thermal degradation of uncured lab-made control novolac resin with different formaldehyde to phenol molar ratio in the resin formulation](image)

**Figure 5.13.** Thermal degradation of uncured lab-made control novolac resin with different formaldehyde to phenol molar ratio in the resin formulation
The thermal degradation curves of the uncured lab-made control novolac resins (Lab PF 0.6), uncured H₂SO₄ acid-catalyzed liquefied bark novolac resin (LBPF –S 0.6), and uncured HCl acid-catalyzed liquefied bark novolac resin (LBPF-C 0.6) with same formaldehyde to phenol or liquefied bark weight ratio in the resin formulation were shown in Figure 5.14. As seen on the thermal degradation curve of uncured Lab PF 0.6, significant degradation started at 200 °C and about 60% of the total weight was lost below 350 °C with an approximate 25% retained weight at 800 °C indicating that the uncured lab-made control novolac resin was thermally unstable at low temperature. The uncured LBPF-C 0.6 resin had a significant weight loss of 20% between 300 – 400 °C with an approximate 33% retained weight at 800 °C, meaning that the uncured HCl acid-catalyzed liquefied bark novolac resins were thermally stable at temperature below 300 °C. The uncured LBPF-S 0.6 resin showed the best thermal stability among these three resins since there was no sudden weight loss observed in the TGA curve. There was only 10% weight loss occurred between 300-400 °C and the retained weight at 400 °C was about 70%. After 400 °C, sample weight started to decrease gradually to a retained weight of approximately 45% at 800 °C. Overall, the uncured liquefied bark novolac resins showed a higher thermal stability than the uncured lab-made control novolac resins, while the uncured H₂SO₄ acid-catalyzed liquefied bark novolac resin exhibited a higher thermal stability than the uncured HCl acid-catalyzed liquefied bark novolac resin at the same formaldehyde to phenol or liquefied bark weight ratio. This can be explained by the fact that the liquefied bark novolac resins contained liquefied bark components that had higher molecular weight, which would require higher temperature to degrade, compared with the lab-made control novolac resins without any bark components. The H₂SO₄ acid-catalyzed liquefied bark novolac resins had a higher molecular weight than the HCl acid-catalyzed liquefied bark novolac resins due to a higher amount of degraded lignin in the LBPF-S resins; thus LBPF-S resins exhibited a higher thermal stability than the LBPF-C resins. Therefore, the addition of liquefied bark components to the novolac resin formulation had an impact on the resin’s structure and its molecular characteristics when the resins are uncured and in the form of linear thermoplastic polymer.
Figure 5.14. Thermal degradation of uncured lab-made control novolac resin (Lab PF 0.6), uncured H$_2$SO$_4$ acid-catalyzed liquefied bark novolac resin (LBPF –S 0.6), and uncured HCl acid-catalyzed liquefied bark novolac resin (LBPF-C 0.6) with same formaldehyde to phenol or liquefied bark weight ratio in the resin formulation.

Figure 5.15. Thermal degradation of cured and uncured H$_2$SO$_4$ acid-catalyzed liquefied bark novolac resins (LBPF-S 0.8).

The thermal degradation curves of cured and uncured novolac resins were shown in Figure 5.15. Resins cured with the curing agent, HMTA, exhibited a higher thermal stability than the uncured resins, where the cured LBPF-S 0.8 had a retained weight at
approximately 52% and the uncured LBPF-S 0.8 had an approximate 40% retained weight. This could be attributed to the higher cross-linking density in the cured resins.

**Figure 5.16.** Thermal degradation of cured H$_2$SO$_4$ acid-catalyzed liquefied bark novolac resins with different formaldehyde to liquefied bark weight ratios in resin formulation (LBPF-S 0.4, LBPF-S 0.6 and LBPF-S 0.8).

According to the thermal degradation curves of cured H$_2$SO$_4$ acid-catalyzed liquefied bark novolac resin with different formaldehyde to liquefied bark weight ratios in resin formulation (Figure 5.16), the resins with higher formaldehyde usage in formulation showed higher post-cured thermal stability. It is worth to mentioned that major weight loss happened after 400 °C for all the cured LBPF-S resins, which indicated that the thermal stability of the resins had been generally enhanced after the curing process.

The thermal degradation curves of cured lab-made novolac resin (Lab PF 0.4), H$_2$SO$_4$ acid-catalyzed liquefied bark novolac resin (LBPF –S 0.4), and HCl acid-catalyzed liquefied bark novolac resin (LBPF-C 0.4) with same formaldehyde to phenol or liquefied bark weight ratios in resin formulation were presented in Figure 5.17. The cured H$_2$SO$_4$ acid-catalyzed liquefied bark novolac resins had similar thermal degradation curves as the cured HCl acid-catalyzed liquefied bark novolac resins indicating that LBPF-S resins had similar thermal stability as the LBPF-C resins. Both cured LBPF-S
resins and LBPF-C resins had a slightly better thermal stability than the cured lab-made control novolac resins synthesized with same formaldehyde to phenol or liquefied bark weight ratio when the temperature was below 400 °C. The Lab PF resins exhibited a slightly higher thermal stability when the temperature was higher than 400 °C. Overall, the lab-made control novolac PF resins had similar total weight loss as the liquefied bark novolac PF resins during the entire thermal degradation process. Similar results were obtained for the liquefied bark resol PF resins from our previous studies [17, 67]. The introduction of bark component to the resin synthesis did not affect the thermal stability among cured lab-made control novolac resins, cured H₂SO₄ catalyzed liquefied bark novolac resins, and cured HCl catalyzed liquefied bark novolac resins synthesized with the same formaldehyde to phenol or liquefied bark weight ratios because similar post-cured thermal stability was observed for these resins, even though the uncured lab-made control novolac resins had different molecular characteristics and structures from the uncured liquefied bark novolac resins. Despite a higher cross-linked structure was indicated by FTIR for the cured liquefied bark novolac resins and some liquefied bark components may become unstable at high temperatures, the liquefied bark novolac resins had a overall similar post-cured thermal stability to the lab-made control novolac resins.

![Figure 5.17](image)

**Figure 5.17.** Thermal stability of cured lab-made control novolac resin (Lab PF 0.4), H₂SO₄ acid-catalyzed liquefied bark novolac resin (LBPF-S 0.4), and HCl acid-catalyzed liquefied bark novolac resin (LBPF-C 0.4) with same formaldehyde to phenol or liquefied bark weight ratios in resin formulation.
5.3 Conclusions

Liquefied bark novolac resins were found to have higher molecular weights than the lab-made control novolac resin (Lab PF). The $\text{H}_2\text{SO}_4$ acid-catalyzed liquefied bark novolac resins (LBPF-S) had higher molecular weights than the $\text{HCl}$ acid-catalyzed liquefied bark novolac resins (LBPF-C). For the Lab PF resins, different formaldehyde to phenol molar ratios did not affect the curing activity of the resulting resins. However, liquefied bark novolac resins exhibited lower curing activity as the formaldehyde to liquefied bark weight ratio increased in the resin formulation. Moreover, LBPF-S resins had lower curing activity than the LBPF-C resins at all selected formaldehyde to liquefied bark weight ratios. It was found that the increase in formaldehyde to phenol molar ratios or to liquefied bark weight ratios had resulted in higher curing activation energies for all Lab PF resins and liquefied bark novolac resins. Whereas, both LBPF-S and LBPF-C resins showed higher curing activation energies in comparison to the Lab PF resins with the same resin formulation. All Lab PF, LBPF-S and LBPF-C resins had faster curing rates at higher formaldehyde to phenol molar ratios or to liquefied bark weight ratios in the resin formulation. Also, given sufficient thermal energy available, faster curing rates were found in LBPF-S and LBPF-C resins compared with the curing rates of lab-made control novolac resins.

All Lab PF resins, LBPF-S and LBPF-C resins were more thermally stable and had higher retained weight with higher amount of formaldehyde usage in the resin formulation. Both uncured LBPF-S and LBPF-C resins showed higher thermal stability than the uncured Lab PF resins, while the uncured LBPF-S resins were more thermally stable than the uncured LBPF-C resins at the same formaldehyde to phenol molar ratios or to liquefied bark weight ratio. After curing with HMTA, all Lab PF resins, LBPF-S resins and LBPF-C resins exhibited a higher thermal stability than the uncured resins. Overall, liquefied bark novolac resins showed similar post-cured thermal stability to the lab-made control novolac resins.

Furthermore, the FTIR analysis agreed with the resin curing behavior that was observed from the DSC results. By comparing the FTIR spectra between uncured and cured resins,
curing reactions were observed between phenol and HMTA in the Lab PF resins and there were curing reactions happened between liquefied bark components and HMTA or between liquefied bark components in the LBPF-S and LBPF-C resins during the curing process.
Chapter 6

Characterization of Molding Composites from Liquefied Bark Novolac Resins

6.1 Introduction

The utilization of the synthesized bio-based PF novolac resin in thermal molding application was explored in this chapter. The lab-made control novolac PF resins and HCl acid-catalyzed liquefied bark novolac PF resins with formaldehyde to phenol or liquefied bark ratios of 0.6 (Lab-PF 0.6 and LBPF-C 0.6, respectively) were used as the matrix for molding the composites. The maple wood powders were used as filler. The hexamine (HMTA), calcium hydroxide and zinc stearate were the hardener, accelerating agent and lubricating agent, respectively. The molding composites were prepared in three formulas with different resin to filler ratio of 7:3, 5:5, and 3:7. The molding composites were prepared using a Laboratory Molding Press at 190 °C for 15 minutes with thickness control of 3mm. The mechanical properties, water resistance, thermal stability and bonding performance of the molding composites prepared from LBPF-C 0.6 resin were investigated and compared with the reference composites molded using Lab PF 0.6 resin in order to study the impact of liquefied MPB infested lodgepole pine bark components and catalyst types on the performance of corresponding molding composites.

6.2 Results and Discussions

6.2.1 Mechanical Properties

The tensile strength, strain and Young’s modulus (MOE) for the novolac molding composite specimens (Lab-PF-0.6 and LBPF-C-0.6) were presented in Figure 6.1, 6.2, and 6.3 respectively. These experimental data will be compared with the literature value, analyzed and discussed in this section.
Figure 6.1. Tensile strength of the novolac molding composite specimens.

Figure 6.2. Tensile strain of the novolac molding composite specimens.
In Figure 6.1, the tensile strengths of both reference (Lab-PF-0.6) and liquefied bark (LBPF-C-0.6) novolac resin composites molded from three different formulas were presented. For the resin-to-filler ratio of 7:3, the Lab-PF-0.6 composite had higher average tensile strength of 39.51 MPa and LBPF-C-0.6 composite specimen had a comparable average tensile strength of 26.65 MPa. For the composite specimen with resin-to-filler ratio of 5:5, the composite molded with LBPF-C-0.6 novolac resin had higher average tensile strength of 30.45 MPa than the composite molded with Lab-PF-0.6 novolac resin, which had an average tensile strength of 24.39 MPa. For the molding formula with higher filler content (3:7 resin-to-filler ratio), the novolac composite specimens molded using both Lab-PF-0.6 and LBPF-C-0.6 resin had relatively low tensile strength of 18.57 MPa and 13.26 MPa accordingly. In general, the tensile strengths obtained from novolac composite with bark component are comparable to the tensile strength of the reference lab novolac composite and higher resin content in the composite gave higher tensile strength. However, it was found that the liquefied bark novolac resin composite with equivalent parts of resin and filler (5:5) had approximately 25% higher tensile strength than the reference lab novolac composite with the same formula. The LBPC-C-0.6 composite sample with 5:5 resin-to-filler ratios also had a greater tensile strength than the LBPC-C-0.6 composite sample with higher resin content.
This result indicated that the tensile strength of the liquefied bark novolac resin composite was formula-dependent. Tensile strength and the ability of the molding composite to stretch along the fracture highly depend on the interfacial adhesion between the resin and wood filler [68]. The imperfect interfacial adhesion would create flaws and weak regions on the composite specimen, which would increase the fragility of the composite and lead to breakage at the material interface [68]. This was probably the main reason that H₂SO₄ catalyzed liquefied bark novolac resin (LBPF-S) was failed to mold into composite. Since the LBPF-S resins were partially thermosetted after synthesis, they were not fully melted upon heating, which led to poor interfacial adhesion between resin and wood filler. Composites with higher resin content attained better interfacial adhesion between the fiber and the matrix. Thus, the composite formula with 7:3 resins-to-filler ratio generally had better tensile properties than composite with lower resin content. However, the liquefied bark novolac resin composite with 5:5 resin-to-filler ratio had the highest tensile strength. This might due to the fact that the highly cross-linking structure and longer chain extension of the liquefied bark novolac PF resin increased material’s ability to resist to fracture and therefore increased the tensile strength of the molding composite.

According to the literature, J. Leite [68] molded a novolac composite at 170°C for 15 minutes using a commercial novolac PF resins as matrix and sugar cane pulp as filler. The highest tensile strength was reported as 28 MPa with a molding composition of 29% resin and 69% pulp of 35-80 mesh. H. Etemadi et al. [69] molded the novolac resin composite using a commercial novolac resin reinforced with 20wt% alumina nanoparticles had a tensile strength of 25 MPa. Alma et al. [70] synthesized novolac PF resin using phenolated bark component of various tree barks under sulfuric acid catalysis. For the resin formulated with pine bark component, the molding products obtained by 4wt% H₂SO₄ acid catalyzed PF novolac matrix reinforced with wood filler had tensile strength of 44.72 MPa. In comparison to the literature with similar molding conditions, the tensile strengths of novolac resin composites molded using the HCl catalyzed liquefied bark novolac PF resin (LBPF-C-0.6) are within the expected range. The LBPF-C-0.6 resin composite with 5:5 resin-to-filler ratio had better tensile property than some
of the commercial novolac resin composite that was reported in the literature [68 - 70]. This indicated that the liquefied bark component in the resin enhanced the mechanical property of the resin composite depending on the composite formula. Moreover, wood powder had good compatibility with both Lab PF novolac resin and LBPF novolac resin, and played an effective role in reinforcing the composite during molding.

**Figure 6.2 & 6.3** showed the tensile strain and Young’s modulus (MOE) of the novolac molding composites. Both graphs followed the same trend as observed in the tensile strength graph (**Figure 6.1**). Molding composites with higher resin content generally had higher tensile strain and Young’s modulus. For the composite molded with liquefied bark PF resin (LBPF-C-0.6), sample with 5:5 resin-to-filler ratio showed the highest tensile strain and modulus among other LBPF-C-0.6 composites, which were 0.8 and 3818 MPa accordingly, and higher tensile strain and modulus than the reference Lab PF resin composite molded with same resin and filler content (5:5 resin-to-filler ratio). According to Pan’s study [70 – 73] on the mechanical properties of bio-composite using liquefied wood PF resin, which synthesized and molded using similar condition, our molding composites with HCl catalyzed liquefied bark component exhibited higher Young’s modulus, and therefore better stiffness. The tensile strength, strain and Young’s modulus obtained from LBPF-C-0.6 composites are comparable with those obtained from the reference Lab-PF-0.6 composites indicated that the addition of liquefied bark component into resin synthesis did not jeopardize the mechanical properties of the molding composites of these resins, but also improved the composite’s tensile properties depending on the molding composition.
6.2.2 Water Soaking Test

The dimension stability of the molding composite and change in weight during water soaking for different molding composition was investigated and discussed in this section.

![Figure 6.4](image)

**Figure 6.4.** Thickness swelling of novolac molding composite specimen.

**Figure 6.4** showed the dimensional change of novolac molding composite specimen in 336 hours (14 days) in terms of thickness swelling for different molding composition. Overall, the thickness of all composite samples had the most visible change in the first 24 hour. According to the results (**Figure 6.4**), the liquefied bark PF (LBPF-C-0.6) novolac composite with resin-to-filler ratio of 7:3 showed the best ability to resist dimensional change when immersed in water with an overall thickness change of 0.48% at the equilibrium. The thickness swelling of both LBPF-C-0.6 molding composite with resin-to-filler ratio of 7:3 and 5:5 reached their equilibrium value (0.48% and 0.83% respectively) after 24 hours of soaking. For the reference composite (Lab-PF-0.6) with resin-to-filler ratio of 7:3 and 5:5, the thickness of composite samples tend to stay constant after 48 hours; however, a noticeable decrease in thickness was observed after 144 hours of soaking and then reached the equilibrium thickness swelling value of 1.5% and 2.3% respectively. The molding composition with 3:7 resin-to-filler ratio had the
least dimensional stability for both LBPF-C-0.6 and Lab-PF-0.6 molding composites with an equilibrium thickness change at 5.03% and 5.55% accordingly. The data collected from the samples with 3:7 resin-to-filler ratio showed a descending trend in thickness change with fluctuated value, which indicated that the PF novolac molding composites with high content of wood filler were not stable while immersed in water for a long period of time. According to the results of thickness swelling test, LBPF-C-0.6 molding composite showed better resistance to dimensional change than the reference Lab-PF-0.6 composites when soaking in water. Some previous studies [64] from our research group on the phenol-formaldehyde resol resins derived from liquefied lodgepole pine barks showed enhanced wet bonding strength and higher lap shear strength than the commercial and reference lab PF resins after both water-soaking-and-drying (WSAD) and boiling water treatment (BWT)/wet tests, which is consistent with the findings in this study. Li et al. [74] revealed that the procyanidin-type condensed tannin-polyethylenimine (PEI) resins were very water-resistant, which might due to the strong adhesion of the resin to wood components caused by the hydrogen bonds between the tannin-PEI network and wood veneer. The catechol moiety of condensed tannins in bark can form strong hydrogen bond with hydroxyl groups of wood components, which will give the tannin-PEI resins a water-insoluble three-dimensional structure and lead to the good water-resistance in the resulting composite [74]. Moreover, the bio-composite with liquefied wood PF resin prepared by Pan et al. [71 – 73] showed poor water-resistance, which might caused by the hydrophilic liquefied wood component in the LWPF resin. In comparison to Pan’s results [71 – 73], our molding composite exhibited a lower thickness swelling, therefore better water resistance. This may be attributed to the fact that the liquefied bark component in the resin enhanced resin’s water-resistance. The liquefied beetle infested pine bark contained very high lignin content. Lignin is an intrinsically hydrophobic polymeric material with desirable phenolic nature that can partially replace phenol to react with formaldehyde during the resin synthesis. The high lignin content in the LBPF-C-0.6 resin might contribute to the good water resistance of the resin. According to our previous study, acid catalyzed liquefied bark PF novolac resin contained higher molecular weight components from liquefied bark. Thus, LBPF resin had a higher molecular weight and more complex three-dimensional crystalline structure.
than Lab-PF resin, which might improve the resin’s resistant to water. Moreover, barks contain more tannin than wood in general [5], which the catechol moiety from the condensed tannin in bark can form strong hydrogen bond with the hydroxyl groups of wood filler that can result in the water-insoluble three-dimensional network in the LBPF resins and therefore enhance the water-resistance in the resulting composite.

Figure 6.5. Weight change of novolac molding composite specimen.

The weight change of novolac molding composite specimen caused by water absorption was present in Figure 6.5. Following the same trend as the thickness-swelling graph, most of the water was absorbed by composite samples in the first 24-48 hours; however the water absorption continued to increase between each 24 hours time interval until reached the equilibrium value after 336 hours. Similar trends in weight change were observed for Lab-PF-0.6 composite with 7:3 resin-to-filler ratio and LBPF-C-0.6 composite with resin-to-filler ratio of 7:3 and 5:5, which reached an overall weight change at 6.92 wt.% 6.98 wt.% and 7.97 wt.% accordingly after 336 hours. There was a noticeable weight loss after 168 hours for composites of Lab-PF-0.6 with all three resin-to-filler ratios, which explained the sudden decrease in thickness after 168 hours of soaking in the thickness-swelling test for the reference Lab-PF-0.6 composites. It was
observed that the Lab-PF-0.6 composites start to decompose and loosen after 168 hours, which may cause the sudden decrease in sample weight and thickness. This indicated that the Lab-PF-0.6 composites had weaker resistant to water. The molding composites with 3:7 resin-to-filler ratio had the highest water absorption, which agreed with the results from thickness swelling test. Moreover, the thickness of composites were stabilized to equilibrium after 168 hours while the weight of composite continued to change. The continuous weight change in composite sample might due to the fact that water was filling the void space between wood filler and resin particle without causing the change in dimension.

In general, composite sample with higher resin content exhibited less water absorption and less change in dimension since there was less wood powder in the composite compositions. PF novolac resin acquired a complex and highly cross-linking three-dimensional polymer structure during the curing process, which might result in excellent resistant to water. The wood fillers in the composite are hydrophilic materials, which absorb water and cause the change in sample weight and dimension. According to the study by George [75], cellulose in wood powder is intrinsically hydrophilic so that chemical treatment is needed to reduce the hydrophilicity of wood in which the hydroxyl group of the cellulose can react with the functional groups of the coupling agent and resin, to achieve a enhanced interaction between fiber and resin by reducing the contact between water molecule and wood particle. Therefore, the high value of water absorption and change in thickness obtained by the composite with higher filler content are expected due to the weak interfacial adhesion between the resin and the filler.

6.2.3 Thermal Stability of the Molding Composites

The thermal stability of the molding composites was tested using the thermal gravimetric analyzer (TGA). The thermal degradation curves of all tested composite samples that molded with HCl catalyzed liquefied novolac PF resins (LBPF-C) or lab-made control novolac PF resins (Lab-PF) at different resin-to-filler ratios (7:3, 5:5, and 3:7) were shown in Figure 6.6. In general, both LBPF-C composites and Lab-PF composites molded with resin-to-filler ratios of 7:3 and 5:5 exhibited similar thermal stability below
400°C, while both molding composites with 3:7 resin-to-filler ratio had a significant weight loss starting at around 250°C and lost approximately 45% of the total weight below 400°C. Composite molded with Lab-PF resin at the resin-to-filler ratio of 7:3 exhibited the best thermal stability among all the testing composites.

![Figure 6.6](image)

**Figure 6.6.** Thermal degradation of molding composites molded with HCl acid-catalyzed liquefied novolac PF resins (LBPF-C) or lab-made control novolac PF resins (Lab-PF) at different resin-to-filler ratios (7:3, 5:5, and 3:7).

The comparison of thermal degradation between the composites molded with HCl catalyzed liquefied novolac PF resins (LBPF-C) and lab-made control novolac PF resins (Lab-PF) at the same resin-to-filler ratios were presented in Figure 6.7-6.9. The molding composites produced from lab-made control novolac PF resins exhibited a better thermal stability than the composites made with HCl catalyzed liquefied novolac PF resins at all selected resin-to-filler ratios. For the composites formulated with resin-to-filler ratio of 7:3 (Figure 6.7), major weight loss was observed at around 300°C for both LBPF-C and Lab-PF composites with a retained weight of 70% and 75% respectively at 400°C. Composites molded with resin-to-filler ratio of 5:5 (Figure 6.8) exhibited very similar thermal degradation curve for both LBPF-C and Lab-PF composites with a retained weight of 68% and 70% accordingly at 400°C. Both LBPF-C and Lab-PF composites
made with 3:7 resin-to-filler ratios had poor resistance against high temperature (Figure 6.9), where a significant weight loss happened at around 250°C and almost half of the total weight was lost below 400°C leaving with 56% and 58% retained weight at 400°C respectively. In the synthesis of the lab-made control novolac PF resin, phenol reacted with formaldehyde under acidic condition and the resulting Lab PF resins acquired a regular linear structure with repeating units. The HCl catalyzed liquefied bark was utilized partially as the phenol substitute in the formulation of LBPF-C resins. Phenolated liquefied bark contains more complex functional groups (i.e. methylol groups) due to the higher lignin content in bark. The resulting LBPF-C resins might contain more complex phenolated structures due to the liquefied bark components in the resin formulation and these components might have less resistance against high temperature. As a result, the LBPF-C resins composites might not have a better thermal stability than the Lab PF resin composites due to its more complicated structure. Therefore, it is understandable that Lab PF resin molding composites showed a slightly better thermal stability than the LBPF-C resin molding composites with higher matrix content at a resin-to-fillers ratio of 7:3. However, LBPF-C resin molding composites had a thermal stability very comparable to Lab PF resin composites at resin-to-fillers ratio of 5:5 and 3:7.

![Figure 6.7](image.png)

**Figure 6.7.** Thermal degradation of molding composites molded with HCl acid-catalyzed liquefied novolac PF resins (LBPF-C) or lab-made control novolac PF resins (Lab-PF) at the resin-to-filler ratios of 7:3.
Figure 6.8. Thermal degradation of molding composites molded with HCl acid-catalyzed liquefied novolac PF resins (LBPF-C) or lab-made control novolac PF resins (Lab-PF) at the resin-to-filler ratios of 5:5.

Figure 6.9. Thermal degradation of molding composites molded with HCl acid-catalyzed liquefied novolac PF resins (LBPF-C) or lab-made control novolac PF resins (Lab-PF) at the resin-to-filler ratios of 3:7.
The thermal degradation of composites molded with HCl catalyzed liquefied novolac PF resins (LBPF-C) at different resin-to-filler ratios of 7:3, 5:5, and 3:7 were shown in Figure 6.10. It was found that composites formulated with higher resin-to-filler ratios exhibited a better thermal stability. Same trend was observed for composites molded lab-made control novolac PF resins (Lab-PF) at different resin-to-filler ratios of 7:3, 5:5, and 3:7 (Figure 6.11). According to the literature [76], wood filler starts to degrade at a relatively low temperature, approximately 200°C. However, both lab-made control novolac PF resins and liquefied bark novolac PF resins had good thermal stability according to our previous results. Therefore, it is understandable that composites molded with higher matrix amount would acquire a better thermal stability.

Figure 6.10. Thermal degradation of molding composites molded with HCl acid-catalyzed liquefied novolac PF resins (LBPF-C) at different resin-to-filler ratios (7:3, 5:5, and 3:7).
6.4 Scanning Electron Microscopy (SEM) results

The fractured surfaces of the molding composites have been investigated using the Scanning Electron Microscopy (SEM) in order to study the interactions between matrix and fibers. The SEM micrograph of the fractured surfaces of the Lab PF resin molding composite at the resin-to-filler ratio of 7:3 was shown in Figure 6.12. At x600 magnification (Figure 6.12-A), it was evident that fibers were broken instead of pulling out because the drawn fiber length was relatively short and broken fibers were exposed at the fracture surface. A closer observation at x1000 magnification (Figure 6.12-B) exposed the severely broken fiber on the fracture surface of the composite. There were obvious remaining matrix attached to the drawn fiber surfaces, which indicates there was a strong interaction between the Lab PF resin and the wood fillers. The SEM micrograph of the fractured surfaces of the LBPF-C resin molding composite at the resin-to-filler ratio of 7:3 was shown in Figure 6.13. Although few broken fibers were exposed on the fracture surface, several smooth channels were observed at x600 magnification (Figure 6.13-A) revealing that several fibers were pulled out during the tensile test rather than
breaking into fractures with shorter length, which indicates a weaker interaction between fiber and matrix. By studying the observation at a higher magnification (Figure 6.13-B), some broken fibers were remained in the channel, which suggested that those fibers were not entirely pulled out during the mechanical test. Thus, effective adhesion existed between the resin and wood fillers in the LBPF-C resin composite at the resin-to filler ratio of 7:3. By comparing Figure 6.12 and Figure 6.13, despite the fact that the fracture surfaces of both Lab PF resin molding composites and LBPF-C resin molding composites were covered mostly by the matrix, the amount of severely broken fibers found on the fractured surface of LBPF-C molding composites were not significant compared with Lab PF resin molding composites. Moreover, several channels were observed in LBPF-C molding composite meaning fibers were pulled out from the matrix whereas fiber pullout tunnels were rarely appeared in the Lab PF molding composites, which further proved the weaker interaction between fiber and matrix in the LBPF-C resin molding composite at the resin-to-filler ratio of 7:3. The results agreed with our mechanical test results where the Lab PF resin molding composite had a higher tensile strength at the resin-to-filler ratio of 7:3, which could be attributed to the stronger interaction between the matrix and the wood fillers in the Lab PF resin molding composite.
Figure 6.12. SEM micrographs of the fractured surfaces of the Lab PF resin molding composite at the resin-to-filler ratio of 7:3.
Figure 6.13. SEM micrographs of the fractured surfaces of the LBPF-C resin molding composite at the resin-to-filler ratio of 7:3.
The SEM micrograph of the fractured surfaces of the Lab PF resin molding composite at the resin-to-filler ratio of 5:5 was shown in Figure 6.14. It was demonstrated in Figure 6.14-A that large amount of visible long tunnels were appeared in the SEM micrograph at x600 magnification, which suggested that a number of fibers have been entirely pulled out instead of breaking during the tensile test. By looking closely on the smooth tunnel at x1000 magnification (Figure 6.14-B), it was confirmed that fibers were smoothly drawn out suggesting that fibers were weakly attached to the matrix in the molding composite. The SEM micrograph of the fractured surfaces of the LBPF-C resin molding composite at the resin-to-filler ratio of 5:5 was shown in Figure 6.15. It can be seen that there were several channels and some broken fibers appeared on the SEM micrograph at x600 magnification (Figure 6.15-A). However, a closer observation at x1000 magnification reveals that fibers were not smoothly pulled out from the matrix since there were broken fiber retentions attached along the pullout channels at the fracture surface. This implied a relatively stronger interaction between matrix and fibers in the LBPF-C resin molding composites at the resin-to-filler ratio of 5:5. As mentioned before, wood fillers were added in the molding composite for reinforcement purpose. If the fiber contents were too high in the composite, cluster of fibers might form during the molding process and fibers could not be evenly dispersed in matrix. Moreover, LBPF-C resins were acquired in solid form after the resin synthesis, which might result in unequal molecular size in resin structure. Thus, if the fiber contents were low, the amount of fibers might be insufficient to be evenly distributed in the matrix and fibers might not play an effective role in reinforcing the molding composites. The uneven dispersion of fibers in the molding composite would lead to poor mechanical properties. Therefore, the mechanical strengths of the molding composites were formula dependent. The result also agreed with the mechanical test results, which the LBPF-C resin molding composites exhibited higher tensile strength than Lab PF resin molding composites at the resin-to-filler ratio of 5:5 and the best tensile property among all LBPF-C resin molding composites with different the resin-to-filler ratios.
Figure 6.14. SEM micrographs of the fractured surfaces of the Lab PF resin molding composite at the resin-to-filler ratio of 5:5.
Figure 6.15. SEM micrographs of the fractured surfaces of the LBPF-C resin molding composite at the resin-to-filler ratio of 5:5.
The SEM micrographs of the fractured surfaces of the Lab PF resin molding composite and LBPF-C resin molding composite at the resin-to-filler ratio of 3:7 was present in Figure 6.16. The fractured surfaces of both molding composites were very porous and chaotic. It was evident that large amount of pores were existed on the fracture surface, which indicated that most of the fibers were pulled out during the mechanical test. Furthermore, the matrix coverage on the fracture surface was not significant indicating that the interaction between matrix and wood filler was weak, which could be attributed to the high fiber content in the composite formulation. The results were consistent with the mechanical test results, which the molding composites for both resins at the resin-to-filler ratio of 3:7 had the lowest tensile strength.

By comparing the SEM micrographs for Lab PF resin molding composites with different resin-to-filler ratios (Figure 6.12, 6.14 & 6.16), numbers of broken fibers and no obvious channels were observed on the fracture surface of Lab PF molding composite with resin-to-filler ratio of 7:3 indicating good interaction and compatibility between matrix and filler while the fracture surface of Lab PF molding composite with resin-to-filler ratio of 5:5 had several obvious fiber pullout channels suggesting weaker matrix-fiber interaction. Therefore, a stronger interaction between matrix and fibers was found in Lab PF molding composites formulated with higher matrix content, which agreed with the mechanical test that higher resin-to-filler ratios would result in higher tensile strength in Lab PF molding composites. By comparing the SEM micrographs for LBPF-C resin molding composites at different resin-to-filler ratios (Figure 6.13, 6.15 & 6.16), both LBPF-C molding composites with resin-to-filler ratios of 7:3 and 5:5 exhibited visible channels indicating that there were some degree of fiber pullout happened during the mechanical test. This finding was consistent with the results from mechanical test as both LBPF-C molding composites with resin-to-filler ratios of 7:3 and 5:5 had similar tensile strength. Moreover, both Lab PF resin and LBPF-C resin molding composite at the resin-to-filler ratio of 3:7 demonstrated the weakest interaction between matrix and fibers.
Figure 6.16. SEM micrographs of the fractured surfaces of the Lab PF resin molding composite and LBPF-C resin molding composite at the resin-to-filler ratio of 3:7

6.3 Conclusions

The synthesized bio-based hydrochloric acid-catalyzed liquefied bark novolac PF resins were suitable for preparing molding composites. However, the sulfuric acid-catalyzed novolac resin was failed to make molding composites. In general, the tensile strengths
obtained from novolac composite with HCl acid-catalyzed bark component are comparable to the tensile strength of the reference lab-made control novolac composite and higher resin content in the composite gave higher tensile strength. However, it was found that the LBPF-C-0.6 resin composite with equivalent parts of resin and filler (5:5) had approximately 25% higher tensile strength than the reference Lab-PF-0.6 resin composite with the same formula, which indicated that the tensile strength of the HCl acid-catalyzed liquefied bark novolac resin composite was formula-dependent. Both tensile strain and Young’s modulus (MOE) of the resulting LBPF-C and Lab PF molding composites followed the same trend as the tensile strength results. The tensile strength, strain and Young’s modulus obtained from LBPF-C-0.6 composites are comparable with those obtained from the reference Lab-PF-0.6 composites indicated that the addition of liquefied bark component into resin synthesis did not jeopardize the mechanical properties of the resulting molding composites, but also improved the composite’s tensile properties depending on the molding composition.

According to the results of thickness swelling test, LBPF-C-0.6 molding composite exhibited better resistance to dimensional change compared with the reference Lab-PF-0.6 composites when soaking in water, which indicated that liquefied bark components in the resin enhanced resin’s water-resistance. In general, composite sample with higher resin content had less water absorption and less change in dimension since there were less wood powders in the composite compositions. Novolac PF resin acquired a complex and highly cross-linking three-dimensional polymer structure during the curing process, which might result in the excellent water resistance.

Moreover, the molding composites produced from LBPF-C-0.6 resins exhibited comparable thermal stability to the Lab-PF-0.6 resins composites at all selected resin-to-filler ratios. It was found that composites formulated with higher resin-to-filler ratios exhibited a better thermal stability. The bonding performance of the synthesized resin was tested by the scanning the fracture surface of the molding composites using the SEM, and results from the SEM micrographs agreed with the mechanical test that higher resin-to-filler ratios would result in better mechanical properties in molding composites.
Chapter 7

Conclusions and Future Works

7.1 Major Contributions

This thesis demonstrates a comprehensive and systematic study on utilizing the sulfuric acid or hydrochloric acid catalyzed liquefied mountain pine beetle (MPB) infested lodgepole pine barks as partial substitutes of petroleum-based phenol in the bio-based novolac PF resins formulation. The properties and characteristics of the synthesized bio-based novolac resin and its potential industrial application in thermal molding are investigated in this study.

The major results and contributions of this thesis study were summarized as following:

1. The acid-catalyzed bark phenol liquefaction is an effective method to convert mountain pine beetle (MPB) infested lodgepole pine bark into suitable phenol substitute, which can be used as alternative feedstock to partially replace the petroleum-based phenol in the novolac PF resin formulation. The change in the catalyst type significantly affects the liquefaction yield, free phenol content of the liquefied bark fraction, properties and characteristics of the resulting liquefied bark component and the unliquefied residues. Both sulfuric acid and hydrochloric acid can effectively catalyze the bark-phenol liquefaction to obtain adequate phenol substitute with the maximum yield of 88.1% and 69.8% respectively. Sulfuric acid catalyst is found to be more effective in bark phenol liquefaction, which results in a higher liquefaction yield and a lower free phenol content in the liquefied bark fraction as well as lower residue content in comparison to the hydrochloric catalyzed bark phenol liquefaction.

2. Both sulfuric acid-catalyzed liquefied bark and hydrochloric acid-catalyzed liquefied bark can be used to synthesize the bio-based liquefied bark novolac PF resin. The bio-based liquefied bark novolac PF resins have higher molecular weights than the lab-made control novolac resin, while H₂SO₄ acid-catalyzed
liquefied bark novolac resins (LBPF-S) have a higher molecular weight than HCl acid-catalyzed liquefied bark novolac resins (LBPF-C) at all formaldehyde to phenol molar ratios or to liquefied bark weight ratios. Both autocatalytic and nth-order cure mechanisms are found in the bio-based liquefied bark novolac PF resins. The liquefied bark novolac resins exhibit lower curing activity as the formaldehyde to liquefied bark weight ratio increases in the resin formulation. The H_2SO_4 acid-catalyzed liquefied bark novolac PF resins have lower curing activity than the HCl acid-catalyzed liquefied bark novolac PF resins at all selected formaldehyde to liquefied bark weight ratios. The liquefied bark novolac resins show higher curing activation energies than the lab-made control novolac resins with the same resin formulation. Moreover, faster curing rates are found in the liquefied bark novolac resins in comparison to the lab-made control novolac resins with sufficient thermal energy available.

3. The uncured liquefied bark novolac PF resins show a higher thermal stability than the uncured lab-made control novolac resins, while the uncured H_2SO_4 acid-catalyzed liquefied bark novolac resin are more thermally stable than the uncured HCl acid-catalyzed liquefied bark novolac resin at the same formaldehyde to phenol molar ratios or to liquefied bark weight ratio. After curing with HMTA, both lab-made control novolac resins and liquefied bark novolac resins exhibit similar post-cured thermal stability.

4. The synthesized bio-based hydrochloric acid-catalyzed liquefied bark novolac PF resins are suitable for preparing molding composites. The sulfuric acid-catalyzed novolac resin is failed to make molding composites. In general, the tensile strengths, strain and Young’s modulus obtained from the bio-based novolac composite with liquefied bark component are comparable to those obtained from the reference lab-made novolac composite, which indicates that the addition of liquefied bark component into resin synthesis did not jeopardize the mechanical properties of the molding composites of these resins. However, the mechanical properties of the liquefied bark novolac resin composite are formula-dependent.
5. The bio-based novolac composite with liquefied bark components showed better resistance to dimensional change in water compared with the reference lab-made novolac composites indicating that liquefied bark components in the resin enhance resin’s water-resistance. The bio-based novolac composite with liquefied bark components exhibited comparable thermal stability to the reference lab-made novolac composites at all selected resin-to-filler ratios.

Both sulfuric acid and hydrochloric acid are suitable to catalyze the bark-phenol liquefaction and successfully converted the mountain pine beetle infested lodgepole pine barks into adequate phenol substitute to partially replace the petroleum-based phenol in the bio-based novolac PF resin synthesis. The synthesized bio-based novolac PF resins have higher molecular weight, more complex structures and comparable resin characteristics, curing performance and thermal stability to the reference lab-made control novolac PF resins, which do not contain liquefied bark components. The hydrochloric acid-catalyzed liquefied bark novolac PF resin can be molded into composites with comparable mechanical properties, thermal stability, bonding performance, and enhanced water resistance to the lab-made control novolac molding composites. Therefore, it is clear that the bio-based novolac PF resins with liquefied MPB infested lodgepole pine bark have good promises for the industrial application in the future.

Moreover, according to Y. Zhao et al.’s study [17] on the characterization of resol PF resins derived from sulfuric-acid catalyzed liquefied MPB infested and non-infested lodgepole pine barks, it was reported that the beetle infestation did not have negative effects on the properties and characteristics of the resulting resins. Thus, the above study on the bio-based novolac PF resins derived from the MPB infested lodgepole pine barks should be applicable for non-infested lodgepole pine bark.
7.2 Future Works

Future studies could focus on improving the performance of the bio-based phenol formaldehyde novolac resins and explore the applications of these bio-based PF novolac resins in other areas.

- As mentioned earlier, the properties of liquefied bark components were wood species dependent. Thus, other wood species, such as non-infested lodgepole pine, spruce, maple, oak, aspen, and other largely available tree species in Canadian forests, or more than one wood species could be incorporated into the formulation of bio-based PF novolac resins.
- Since both sulfuric acid and hydrochloric acid are strong and corrosive mineral acids, it would be more environmentally friendly to replace these strong acid catalysts with some weak acids, such as acetic acid or oxalic acid. Bark phenol liquefaction under weak acid catalysis for obtaining suitable partial phenol substitute in bio-based PF novolac resin synthesis could be further studied.
- It would be essential to further investigate the resin formulation and optimize the synthetic condition in order to improve the performance of the resulting bio-based novolac PF resin for the commercialization purpose. Different phenol to bark molar ratio in bark phenol liquefaction, liquefaction conditions (such as time, temperature, catalyst types and etc.), partial phenol substitution in novolac PF resin synthesis, reaction condition for resin synthesis (such as time, temperature, and etc.), and etc. should be examined in the future.
- It would be interesting to explore the applications of this novel bio-based PF novolac resin in areas other than thermal molding industry.
- It would be necessary to conduct economic analysis and life cycle analysis on this bio-based PF novolac resin in order to test the feasibility for commercialization.
- It would be interesting to explore other types of curing agent, which might be more compatible with the liquefied bark component and result in better curing performance.
Reference


45. C. Mané, N. Sommerer, T. Yalcin, V. Cheynier, R. B. Cole, and H. Fulcrand, “Assessment of the molecular weight distribution of tannin fractions through


