PREPARATION AND CHARACTERIZATION OF FORMALDEHYDE FREE WOOD ADHESIVES LIGNIN EXTRACTED FROM OIL PALM EMPTY FRUIT BUNCH

by

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Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

JULY 2015
ACKNOWLEDGEMENTS

Praise is due to Allah Whose worth cannot be described by speakers, Whose bounties cannot be counted by calculators and whose claim (to obedience) cannot be satisfied by those who attempt to do so, Whom the height of intellectual courage cannot appreciate, and the divings of understanding cannot reach; He for whose description no limit has been laid down, no eulogy exists, no time is ordained and no duration is fixed. First of all, the best thanks and praise to Allah almighty, who helped me and make it easy for me to reach this goal. First and foremost, I would like to express my deepest gratitude and sincere thanks goes to my supervisor, Assoc. Prof. Afidah Abdul Rahim and Assoc. Prof. Mohamad Nasir Mohamad for giving me an opportunity to work in their laboratory during my study and giving me their invaluable guidance, continuous encouragement and generous support throughout this work. I would like to express my deepest gratitude to the government of Iraq, the government of Malaysia, Materials Research Directorate, Ministry of Science and Technology, Iraq, and Universiti Sains Malaysia for the financial and technical supports. My grateful acknowledgement to Universiti Sains Malaysia of funding this research project under RU grants 1001/PKIMIA/854002. I would also like to thank all staff members of Institute of Postgraduate Studies (IPS), the School of Chemical Sciences, School of Physics and School of Biological Sciences-USM for their help and for the use of necessary equipments. I wish to express my warm and sincere thanks to all my best colleagues and friends. Thank you Dr. Adel Mostafa Kamel for his encouragement. My heartfelt gratitude towards my family: particularly my loving wife, my daughters (Manar, Aya, Yamam), my brothers and my sisters, for their continuous love, prayer, support and patience throughout my PhD study. Thank you all.
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<td>AEL</td>
<td>Autocatalyzed ethanol lignin</td>
</tr>
<tr>
<td>ASAM</td>
<td>Alkaline Sulfite Anthraquinone Methanol</td>
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<td>BT</td>
<td>Bentonite</td>
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<td>BWT</td>
<td>Boiling water test</td>
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<tr>
<td>CEC</td>
<td>Cation exchange capacity</td>
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<td>CPF</td>
<td>Commercial phenol formaldehyde</td>
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<tr>
<td>DBE</td>
<td>Double bond equivalent</td>
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<td>DMSO-d₆</td>
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<td>Hexamethylenetetramine</td>
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<td>Description</td>
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<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>KL</td>
<td>Kraft lignin</td>
</tr>
<tr>
<td>LPF</td>
<td>Lignin-phenol formaldehyde resin</td>
</tr>
<tr>
<td>MAP</td>
<td>Marine adhesive proteins</td>
</tr>
<tr>
<td>MF</td>
<td>Melamine formaldehyde resin</td>
</tr>
<tr>
<td>MMT</td>
<td>Montmorillonite</td>
</tr>
<tr>
<td>MTGKL</td>
<td>Modified tannin glyoxalated Kraft lignin</td>
</tr>
<tr>
<td>MOE</td>
<td>Modulus of elasticity</td>
</tr>
<tr>
<td>MOR</td>
<td>Modulus of rupture</td>
</tr>
<tr>
<td>MPB</td>
<td>Mountain pine beetle</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>ODA</td>
<td>Octadecylamine</td>
</tr>
<tr>
<td>ODA-BT</td>
<td>Octadecylamine bentonite</td>
</tr>
<tr>
<td>OPEFB</td>
<td>Oil palm empty fruit bunch</td>
</tr>
<tr>
<td>OSB</td>
<td>Oriented strand boards</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyethylenimine</td>
</tr>
<tr>
<td>PF</td>
<td>Phenol formaldehyde resin</td>
</tr>
<tr>
<td>PLS</td>
<td>Polymer/layered silicate</td>
</tr>
<tr>
<td>pMDI</td>
<td>4,4’-diphenylmethane diisocyanate</td>
</tr>
<tr>
<td>PO</td>
<td>Propylene oxide</td>
</tr>
<tr>
<td>PPO</td>
<td>Polypropylene oxide</td>
</tr>
<tr>
<td>pTSA</td>
<td>Para-toluene sulfonic acid</td>
</tr>
<tr>
<td>Rp</td>
<td>Polarization resistance</td>
</tr>
<tr>
<td>S</td>
<td>Syringyl</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>SSL</td>
<td>Spent sulfite liquor</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>TGKL</td>
<td>Tannin glyoxalated Kraft lignin</td>
</tr>
<tr>
<td>TGLP</td>
<td>Tannin glyoxalated lignin polyols</td>
</tr>
<tr>
<td>TGLW</td>
<td>Tannin glyoxalated liquefied wood</td>
</tr>
<tr>
<td>UF</td>
<td>Urea formaldehyde resin</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic chemic</td>
</tr>
<tr>
<td>WSAD</td>
<td>Water-soaking-and-drying</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
LIST OF SYMBOLS

\( d \)  
Basal spacing

\( \text{M}_n \)  
Number average molecular weight

\( \text{M}_w \)  
Weight average molecular weight

\( \text{M}_w/\text{M}_n \)  
Polydispersity

\( T_{\text{g}} \)  
glass transition temperatures

\( T_{\text{max}} \)  
Maximum degradation temperature

\( T_{\text{onet}} \)  
Onset temperature

\( \text{Wt}\% \)  
Weight percentage

\( \theta \)  
Diffraction angle

\( \lambda \)  
Wavenumber
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ABSTRAK

penyelidikan ini, lignin/tanin mesra alam dan cecair perekat berasaskan kayu-OPEFB telah dikaji dengan untuk menyediakan perekat kayu bebas formaldehid dan untuk meningkatkan komposisi bahan-bahan mesra alam yang boleh diperbaharui dalam formulasi pelekat kayu. Buah tandan kosong kelapa sawit (OPEFB) telah digunakan sebagai bahan mentah dalam. Proses delignifikasi OPEFB telah dijalankan menggunakan pulpa Kraft dan pulpa auto-bermangkinkan etanol-air (organosolv). Poliol lignin telah disediakan daripada pencairan Kraft lignin dan daripada pencairan langsung sisa lignoselulosa OPEFB. Analisis Mannich menggambarkan bahawa lignin Kraft mempunyai jumlah kedudukan gelang aromatik aktif yang agak tinggi (2.99%) berbanding lignin organosolv (2.06%), yang menunjukkan reaksi yang menggalakkan dengan glioksal daripada lignin organosolv. Berat molekul purata produk cecair mempamerkan peningkatan yang signifikan dengan proses pencairan lignin (16427 g mol⁻¹) dan dengan proses pencairan langsung OPEFB (12203 g mol⁻¹) berbanding dengan Kraft lignin (1564 g mol⁻¹). Ciri-ciri ini mengesahkan kejayaan penyediaan produk lignin poliol yang disasarkan. Pengubahsuaian tanin menggunakan poli berantai (amina-ester) telah dikaji. Spektrum FTIR, ¹H NMR dan ¹³C NMR mengesahkan kejayaan penyediaan poli (amina-ester) dan perekat tanin diubahsuaui/terglioksal lignnin (MTGKL). Spesimen papan lapis dengan resin MTGKL mempamerkan sifat tahan air apabila direndam di dalam air paip selama 24 jam, tanpa pengelupasan dalam mana-mana spesimen
PREPARATION AND CHARACTERIZATION OF FORMALDEHYDE FREE WOOD ADHESIVES LIGNIN EXTRACTED FROM OIL PALM EMPTY FRUIT BUNCH

ABSTRACT

In this work, environment-friendly lignin/tannin and liquefied OPEFB-based wood adhesives have been studied to prepare formaldehyde-free wood adhesives and to increase the proportion of renewable environmentally friendly materials in these wood adhesive formulations. The oil palm empty fruit bunch (OPEFB) was used as raw material. The delignification processes from OPEFB were conducted using Kraft pulping and auto-catalyzed ethanol–water (organosolv) pulping. Lignin polyols were prepared from the liquefaction of Kraft lignin and from the direct liquefaction of OPEFB lignocellulosic waste. The Mannich reactivity analysis illustrated that the Kraft lignin has comparatively higher amounts (2.99%) of activated free aromatic ring positions compared with organosolv lignin (2.06%), suggesting favourable reaction with the glyoxal than organosolv lignin. The average molecular weight of liquefied product exhibited significant increase with lignin liquefaction process (16427 g mol⁻¹) and with the direct liquefaction process of OPEFB (12203 g mol⁻¹) compared with Kraft lignin (1564 g mol⁻¹), which confirms the successful preparation of targeted lignin polyol products. Modification of tannin using hyperbranched poly (amine-ester) has been studied. FTIR, ¹H NMR and ¹³C NMR spectra confirmed the successful preparation of hyperbranched poly (amine-ester) and modified tannin/glyoxalated lignin adhesive (MTGKL). The plywood specimens with MTGKL resin exhibited water resistant properties when soaked in tap water for 24 hours, where no delamination occurred in any of the specimens while delamination
of TGKL plywood resin specimen was evident. The lignin based-wood adhesives was also evaluated in boiling water after the modification of lignin polyols/tannin adhesive (TGLP) with polyethyleneimine (PEI). At 10% of PEI with TGLP resin, the delamination of plywood specimens did not occur after exposure in the tap water and boiling water. In the same context, this work demonstrates the possibility of synthesizing water resistant wood adhesives from the liquefaction of OPEFB in the presence of glyoxal as a curing agent that meets the requirements of relevant international standards for the manufacture of plywood. The FTIR spectra confirmed the reaction between liquefied OPEFB and glyoxal through the presence of C-C, C-O-C, and C=O groups in the resol structure. Tensile strength tests clearly demonstrated that the tensile strengths for both dry and wet TGLW plywood specimens (21.4 and 19.71 MPa) respectively, surpassed the requirements of relevant international standards. The effect of inorganic and organic clay on the glyoxalated lignin polyol/tannin wood adhesive was also studied. The FTIR, XRD, and SEM characterizations indicated that the modification of bentonite via octadecylamine (ODA) salt occurred. The tensile strengths of TGLP plywood resin specimen increased significantly through the incorporation of low contents of ODA-BT (1, 2, and 3 wt%). Comparison between pure TGLP resin and the composites shows that the thermal stability was decreased.
CHAPTER 1
INTRODUCTION

1.1 General

Wood adhesives have a very important function in the industrial production of wood-based panels. The final performance of wood panels significantly depends on the efficiency of the adhesive. Thus, the success and the evolution of the modern wood panels industry have been largely attributed to the evolution of quality wood adhesives. However, the wood-based panel industry and the adhesive industry both have a high affinity towards creativity.

The use of wood adhesives has a long tradition (Keimel, 2003), with a recorded history that spans at least 3,000 years from the time of the Egyptians (River, 1994; Skeist and Miron, 1990). The evolution of industrial wood adhesives can be explained in two stages. The first stage includes the commonly used adhesives based on natural polymers such as protein, starch, soybean, etc. The main features of this type are its ease of handling and environment friendly properties, but these types of adhesives do not meet the fundamental required bonding strength and water resistance (Charles, 2005; Pizzi and Mittal, 2003). For example, casein glues were widely used in World War I to create the wood-based mainframes of aircrafts. These adhesives lacked water resistance and could be attacked by fungi and microorganisms (mold growth) (Lambuth, 2003; Scields, 1984). Their poor durability limited their use to interior applications (Conner, 2001; Lambuth, 2003; Scields, 1984). In the second stage, condensation resins based on formaldehyde have replaced natural resins; these include urea formaldehyde (UF), phenol formaldehyde (PF), and melamine formaldehyde (MF) resins that usually have better strengths and
water resistances. Condensation resins based on formaldehyde now accounts for the largest volume of wood adhesives. PF resins are highly resistant to the hydrolysis of the C-C bond between the aromatic ring and the methylene bridge. Consequently, these resins are used in moisture- and weather-resistant wood adhesives and boards, such as waterproof plywood, particleboards, and OSBs for use in exterior weather conditions (Charles, 2005; Pizzi and Mittal, 2003).

Synthetic resins derived from fossil fuels will be exhausted and may eventually contribute to CO₂ emissions, thereby influencing climate changes. These materials are non-renewable and toxic. Recent health and environmental concerns include the emission of carcinogenic volatile formaldehyde compounds, as well as the continuous fluctuation of price of oil and its derivatives. Consequently, several studies have been conducted for the development of renewable and inexhaustible natural resources for the reduction or replacement of synthetic adhesives for wood panels, thereby decreasing the emission of formaldehyde (Mozaffar et al., 2004; Nihat and Nilgül, 2002; Pizzi, 1977; Thompson, 1991; Yoosup et al., 2008).

Adhesives based on renewable resources have long been sought. However, their industrial application and large-scale production are still below the level of expectation. The obvious advantages to the use of natural biomaterials are availability, biodegradability, and lower toxicity.

1.2 Biomass

Biomass refers to all animate organic materials, including crops, marine products, and forestry residues (such as tree stumps, branches, and dead trees), as well as some organic wastes such as agricultural waste and municipal solid waste.
(Demirbas and Arin, 2002; Demirbas, 2000). Therefore, a biomass resource includes plant or animal matter, which can be converted into industrial chemicals such as BTX (benzene, toluene and xylene) and polyurethane. Different kinds of plants can be cultivated for biomass, such as hemp, willow, corn, and bamboo, including different tree species such as eucalyptus and oil palm.

Biomass is a promising source of energy that can replace fossil oil. Thus, this material is important in sustainable production because it is renewable and abundant resource on Earth. The annual production of renewable materials is approximately $20 \times 10^{10}$ tons. Only 3% of known renewable materials are used for non-food manufacturing, such as in the pulp and paper industry (Zhang, 2008). Biomass resources are considered to be cheaper than other resources, such as crude oil and natural gas (Zhang, 2008). In addition, the cultivation of plants and the process of burning fuel allows biomass production to have a short cycle. Plant biomass mainly consists of cellulose ($[\text{C}_6(\text{H}_2\text{O})_5]_n$), hemicellulose ($[\text{C}_5(\text{H}_2\text{O})_4]_n$), and lignin ($[\text{C}_{10}\text{H}_{12}\text{O}_3]_n$), with small amounts of pectin, protein, extractives, and ash, as shown in Figure 1.1. Plant biomass is also called lignocellulosic biomass (Pan, 2011).
The available lignocellulosic biomass has several possible applications as raw materials for energy projects, as well as for the chemical industry. Moreover, sustainability requirements and reduced CO$_2$ gas emissions into the atmosphere are important factors when using biomass resources.

Industrial chemicals can be obtained through the thermal depolymerization and decomposition of biomass components, such as cellulose, hemicelluloses, and lignin, in various forms of charcoal, namely, liquid, gas, and solid remnants. The potential chemicals that can be extracted from lignin conversions include methanol, ethanol, mixed alcohols, and hydrocarbons, as well as the byproduct C$_1$ to C$_4$ gases, phenol, substituted phenols, guaiacols, syringols, syringaldehyde, substituted lignins, mixed aromatic polyols, and other chemicals. To date, the wood composite production mainly depends on the petrochemicals derived from fossil oil and condensation of resin-based formaldehydes such as PF and UF resins (Liu & Li 2007).
Environmental concerns have been raised regarding the volatile organic compounds and toxic chemicals in many adhesives, as well as the continuous fluctuations in the prices of oil and its derivatives. Thus, several studies were conducted for the production of environment friendly products from biomass polymers, with a primary focus on lignin derivatives for the production of polymeric compounds, especially phenolic and epoxy resins (Methacanon, 2010; Silva et al., 2009).

Malaysia has more than 4 million hectares of oil palm plantations that yield an estimated amount of 90 million tons of renewable biomass (fronds, trunks, palm press fibers, shells, and empty fruit bunches) generated from the mechanical processes of palm oil production (Malaysia Palm Oil Board, 2013). Unfortunately, oil palm biomass is still treated as a waste, without considering the value of materials such as cellulose, hemicelluloses, and lignin (Mohamad Ibrahim et al., 2006).

Figure 1.2: View of EFB wastes piled up in a palm oil mill premise (Geng, 2013)
The remnants of biomass must be eliminated in a systematic and scientific manner because the presence of such residues is dangerous to the environment. An important element extracted from EFBs is lignin (Mohamad Ibrahim et al., 2008).

1.3 Lignin

Lignin is derived from the Latin term Lignum, which means wood (Sarkanen and Ludwig, 1971). Payen in 1838 first reported the composite nature of wood (McCarthy and Islam, 1999) and referred to the carbon-rich substance as the “encrusting material”, which is an integral part of cellulose in wood. Schulze (1865) later explained that this encrusting material is lignin. Lignin is a complex phenolic polymer that is present in plant tissues. This most abundant and important natural polymer on earth second to cellulose is a byproduct of the pulp and paper industry (Methacanon, 2010; Silva et al., 2009).

Lignin exists in all vascular plants and represents approximately 15 to 30% of the dry mass of wood. Lignin is covalently associated with hemicellulose in plant cell walls. Thus, lignin is crosslinked with a variety of plant polysaccharides. Lignin is characterized by its relatively high strength, rigidity, impact strength, and resistance to ultra-violet light; lignin in wood has a high degree of heterogeneity and lacks a defined primary structure (Belanger et al., 2010). Lignins are natural phenolic materials that are well known for their role in woody biomass to provide resistance to biological and chemical decomposition.

Plant lignins can be generally divided into three classes: hardwood (angiosperm), softwood (gymnosperm), and grass (graminaceous) lignin (Pearl, 1967). Lignin is the most complex of the natural phenolic polymers (Fig. 1.3) and is
described as an amorphous three-dimensional network. The repeated units in the formation of this complex polymer are phenylpropanoid monomers, namely, the coniferyl, sinapyl, and \( p \)-coumaryl alcohols (Hatakeyama et al., 2002; Koullas et al., 2006; Silva et al., 2009; Zakzeski et al., 2010). The phenylpropane unit of lignin is depicted in Figure 1.4.

Figure 1.3: An example of chemical structure of lignin (Adler, 1977)
The bio-structure of lignin is made of the free radical reaction of these monomers to form a stiff, three-dimensional cross-linked matrix (very similar to thermosetting resins such as phenol-formaldehyde resins). The lignin structure is characterized by rigidity to exterior physicomechanical acts, leading to shear stress and deformation. Therefore, these structures need a high flexibility towards the rearrangement of bonds within the lignin network, which leads to more condensed polymers. Chemically, lignin is considered a complex insoluble biopolymers, although many studies have been conducted, its chemistry and molecular biology is still not completely understood (Boerjan et al., 2003).

The lignocellulose complex contains four basic types of bonds: the carbon-to-carbon bonds, ether bonds, ester bonds, and hydrogen bonds. These bonds are responsible for providing linkages between the individual components of lignocellulose (intrapolymer linkages) and link the different components to form the complex (interpolymer linkages). The bonding positions are summarized in Table 1.1 (Faulon et al., 1994).
Table 1.1: Linkages between the monomer units that form the individual polymers lignin, cellulose and hemicellulose, and between the polymers to form lignocellulose (Faulon et al., 1994)

<table>
<thead>
<tr>
<th>Bonds within different components (intrapolymer linkages)</th>
<th>Ether bond</th>
<th>Lignin, (hemi)cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon to carbon</td>
<td>Lignin</td>
<td>Lignin</td>
</tr>
<tr>
<td>Hydrogen bond</td>
<td>Cellulose</td>
<td>Hemicellulose</td>
</tr>
<tr>
<td>Ester bond</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bonds connecting different components (interpolymer linkages)</th>
<th>Ether bond</th>
<th>Cellulose-Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hemicellulose</td>
<td></td>
</tr>
<tr>
<td>Ester bond</td>
<td>Hemicellulose-lignin</td>
<td></td>
</tr>
<tr>
<td>Hydrogen bond</td>
<td>Cellulose-hemicellulose</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hemicellulose-Lignin</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cellulose-Lignin</td>
<td></td>
</tr>
</tbody>
</table>

The main kinds of linkages that connect the monomers within the lignin polymer are carbon-to-carbon bonds and ether bonds (Table 1.1). The total fraction of ether linkages in the lignin molecules accounted for approximately 70% of the total linkages between monomer units. The remaining 30% of the total bonds between the units represent the carbon-to-carbon linkages (Henriksson, 2007). The most common types of linkages which are found in the lignin structure illustrated in Figure 1.5 (Dence and Lin, 1992; Sjöström, 1993). In addition to the predominant linkages, at least 20 different linkage types have been identified (Whetten et al., 1998).

A wide range of functional groups are characterized in lignin. These groups are capable of meeting industrial requirements. The effectiveness of lignin mainly depends on the aliphatic and phenolic hydroxyl groups, as well as the carboxyl groups. These groups vary with the source of lignin and the extraction process used to obtain lignin. The solubility of lignin depends largely on the percentage of these functional groups. Generally, most types of lignin are quite soluble in alkaline solutions as a result of the ionization of carboxyl and hydroxyl functional groups.
(Henriksson, 2007). In the aromatic rings on lignin, only about 10–13% of the phenolic hydroxyl groups are free to form neighboring phenylpropane linkages, whereas the others form ether linkages (Henriksson, 2007). The phenols content is important because it has a major role in chemical reactions, especially in modified lignin because it is the most reactive site in lignin structure.

**Ether linkage**

\[
\begin{array}{c}
\text{C} - \text{O} - \text{C} \\
\text{C} \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{C} - \text{O} - \text{C} \\
\text{C} \\
\text{O} \\
\end{array}
\begin{array}{c}
\text{C} - \text{O} - \text{C} \\
\text{C} \\
\text{O} \\
\end{array}
\]

\(\beta\text{-O-4}\) \hspace{1cm} \(\alpha\text{-O-4}\) \hspace{1cm} 4-O-5

**Carbon - Carbon Linkages**
Lignins are separated from the other parts of the lignocellulosic complex by physical and/or chemical means; these materials can be obtained as by-products of various processes, such as bioethanol production and papermaking. The botanical source affects lignin properties, but the delignification (pulping) process and the extraction procedures significantly affect the lignin structure, purity, and other characteristics (Lora et al., 2008; Lora and Glasser, 2002). Generally, chemical pulping is a way to remove lignin from wood (delignification) by altering the

Figure 1.5: Common intermonomeric linkages in a lignin molecule (Henriksson, 2007)
chemical composition to produce soluble fragments of the polymer. Several different processes are used to produce chemical pulp, but the Kraft pulping process is considered the most common worldwide. To develop a modern paper manufacturing process, the use of the alkaline pulping process with wood as raw material was patented by Hugh and Burgess in 1854 because wood is readily available and fairly inexpensive. In the Kraft pulping process, lignin removal is done by treating wood chips with sodium sulfide under alkaline conditions at elevated temperatures. Kraft delignification occurs by modifying the lignin structure in two different ways. First, the lignin structure is degraded into smaller units by cleaving the linkages of inter-units. Second, the lignin structure is made more soluble in the cooking liquor via the introduction of hydrophilic groups in polymer and cleaved fragments (Gierer, 1980). These phenomena occur when the linkages between phenylpropane units are cleaved to generate free phenolic hydroxyl groups. The existence of these hydroxyl groups increases the hydrophilicity of lignin and lignin fragments; thus, the lignin solubility is increased in the cooking liquor. Meanwhile, the carbon-carbon linkages become more stable and tend to survive in the Kraft pulping process (Sjöström, 1993). During cooking, most of the β-O-4 linkages in lignin structures are hydrolyzed (>95%) and lignin is degraded into fragments of different molecular weights that are soluble in the alkali solution (Gellerstedt and Zhang, 2001). The color of spent liquor from cooking is deep brown because of the lignin fragments. At this point of the process, hemicellulose is still attached to lignin. Figure 1.6 shows the three distinct phases of the dissolution of lignin and hemicellulose.

The initial delignification step occurs at temperatures less than 150 °C; approximately 20% of lignin and carbohydrates are dissolved during this step. Thereafter, at above 150 °C in the bulk phase, approximately 90% of lignin has been
selectively dissolved, without dissolving more carbohydrates. The final delignification step includes final treatment at 170 °C, which would entail the removal of the remaining lignin with a significant loss of carbohydrates (Gellerstedt and Lindfors, 1984). This step can practically stop the cooking procedure of the bulk phase because continuing to the final phase could lead to a loss of quality and low yield. Therefore, the cooking time should be adjusted to achieve the target quality.

![Figure 1.6: The dissolution of lignin and hemicelluloses during Kraft pulping that proceeds in three distinct phases (Gellerstedt and Lindfors, 1984)](image)

The delignification process used for the isolation of lignin has an important role in defining the features of the final structure. To dissolve lignin, nucleophiles, such as hydroxide ions and hydrogen sulfide, are introduced. The cleavage of ether bonds would increase the amount of free phenolic groups.
Kraft lignin has many applications, although most are still in the pilot scale. Products based on Kraft lignin include carbon fibers (Kadla et al., 2002), carriers for pesticides and fertilizers (Zhang, 2008), binders, resins (Tejado et al., 2007), blending materials containing thermoplastic polymers (Gosselink et al., 2005), and ion exchange resins (Zoumpoulakis and Simitzis, 2001).

Organosolv fractionation is one of the promising pretreatment technologies, wherein lignin production relies on the use of systems based on various organic solvents. Moreover, this method has become a subject of much scientific research activities, which generated increasing interest in the paper and pulp industry after the trend to reduce the environmental impact of these materials (Zhao et al., 2009). In the organosolv process, lignocellulosic feedstock is treated with an organic solvent, such as alcohols and organic acids, with the presence of water as a co-solvent to reduce the vapor pressure and lower the pH thereby solubilizing hemicellulose for the extraction of lignin from lignocellulosic biomass. Additionally, the use of organic solvents limits the formation of sulfated byproducts. Compared with other pulping processes, one of the main benefits of organosolv pulping is the highly effective delignification of lignocellulosic feedstock prior to enzymatic hydrolysis, whereas the chemical structure of lignin has been largely preserved and less condensed than other pretreated lignins. In addition to delignification, hemicellulose dissolves in the organic solvent and, thus, improves the enzymatic digestibility of the cellulose fragments to fermentable sugars (Zhao et al., 2009). Another advantage of the organosolv process is the higher purity of retrieved lignin and the absence of sulfonates, which makes it more environment friendly (Pan et al., 2006, 2005; Zhang, 2008).
The organosolv pulping process uses various organic solvents such as aliphatic alcohols (Pan et al., 2006; Solár et al., 2001), diols (Jiménez et al., 2004), organic acids (Ibrahim and Glasser, 1999), and amines (Heitz et al., 1994).

However, the most common organosolv processes are the ethanol organosolv (Alcell) and acetic acid pulping processes. Both contain mineral acids in small amounts, such as sulfuric acid or hydrochloric acid (Acetosolv). Generally, alcohols with low molecular weights are most commonly used in organosolv pulping; in addition, primary alcohols are better agents than secondary or tertiary alcohols for delignification (Zhao et al., 2009). Among the alcohols, the ethanol solvent is the most widely used in organosolv pulping. Given its low toxicity, ease of recovery, and low cost, ethanol is the most preferred alcohol. The Alcell® Process technology was developed in 1990 for industrial scale production in Canada (El Hage, 2012). Organosolv lignin can be used to produce certain valuable products and green materials, such as adhesives (Çetin and Özmen, 2002a), films, fibers (Pereira et al., 2007) and biodegradable polymers (El Hage et al., 2009).

1.4 Tannin

Tannins are polyphenols that exist naturally and are widely distributed in plants. These compounds are water-soluble phenolics with molecular weights ranging from 500 to 3000. In addition, tannins have the capacity to bind with precipitate alkaloids, gelatin, and other proteins (Karamać et al., 2007). Natural tannins are divided into two main classes (Fig. 1.7). The condensed polyflavonoid tannins (proanthocyanidins) are biopolymers based on flavan-3-ol, which would liberate catechins and anthocyanidins as end groups in alcohol solution and at
elevated temperatures. Meanwhile, gallotannins and ellagitannins belong to the group of hydrolyzable tannins. Gallotannins consist of galloyl esters of glucose or quinic acid, whereas ellagitannins are derivatives of hexahydroxydiphenic acid (Hagerman et al., 2005). Chemically and commercially, condensed tannins from natural polymers are more interesting in the production of adhesives and resins. These tannins account for more than 90% of the total world production of chemicals. To precipitate proteins, to reduce the use of vitamins and minerals, and to inhibit digestive enzymes, tannin can be considered an antinutrient compound of plant origin. Several studies have mentioned the antiradical and antioxidant activity of tannins (Alasalvar et al., 2006; Amarowicz, 2007; Amarowicz et al., 2004). Treatment of leathers with natural vegetable tannins in the leather tanning industry provide some advantages, such as more resistant to mechanical ware and less susceptible to biological and other types of attack.

Tannin application in corrosion studies has been investigated by many researches. Mangrove tannin that was extracted from the mangrove bark was used as anticorrosion inhibitors. It has been found that the mangrove tannin effectively inhibits the corrosion on copper metal in hydrochloric acid solution. The results of the electrochemical and weight loss methods showed that the inhibition efficiency of mangrove tannin increases with increased concentrations (Shah et al., 2011). The influence of halide salts viz., KCl, KBr and KI on the corrosion inhibition of mangrove tannin were also investigated. Results show that mangrove tannin alone provided satisfactory inhibition on the corrosion of mild steel and it was also found that the inhibition efficiency increased synergistically in the presence of halide ions (Ridhwan et al., 2012). The synergy between iodide ions and mangrove tannin extracted from mangrove bark (waste products of the charcoal industry) was tested.
on the inhibition of corrosion of mild steel in 0.5 M HCl and 0.25 M H₂SO₄. It was compared with the inhibition provided by mimosa and chestnut tannins. Mangrove tannins showed comparable inhibitive properties to those of commercial mimosa and chestnut tannin (Ridhwan et al., 2015).

<table>
<thead>
<tr>
<th>Basic Unit</th>
<th>Hydrolyzable Tannin</th>
<th>Condensed Tannin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallic acid</td>
<td></td>
<td></td>
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<tr>
<td>Flavone</td>
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</table>

Figure 1.7: Structure of tannin

1.5 **Biomass liquefaction**

Biomass can be converted into liquid or gaseous products, which can be used in organic synthesis or engines of internal combustion (Pan et al., 2009). Generally, the main routes for the production of biofuels and various chemicals from biomass are based on biochemical and thermochemical conversions (Demirbas, 2001).

Thermochemical conversions involve three main processes, namely, gasification, pyrolysis, and liquefaction. Gasification uses heat at temperatures higher than 1000 °C to convert lignocellulosic biomass into synthetic gas with a mixture of CO, H₂, and CH₄, in addition to CO₂ and N₂ (Demirbas, 2001). Pyrolysis involves the thermal decomposition of lignocellulosic biomass by heat in the absence
of O\textsubscript{2} to obtain charcoal (solid), bio-oil (liquid), and fuel gas (Demirbas & Arin, 2002). Thermochemical processes involve two types of liquefaction. The first type is comparable to pyrolysis and called direct liquefaction. However, liquefaction occurs at temperatures between 250 and 350 °C in the absence of O\textsubscript{2} and is usually conducted under pressures of approximately 5–10 MPa (Demirbas, 2000), whereas pyrolysis is conducted at temperatures between 380 °C and 550 °C. The second type of liquefaction process dissolves lignocellulosic biomass in organic solvents with or without a catalyst at moderate temperatures (100–250 °C). Given its simple preparation, high level of production, high energy conversion, and high capacity of organic material treatment, the liquefaction process has attracted more attention (Ye et al. 2014).

Much work has been done on the liquefaction process of biomass in relation to the raw materials, solvents, and catalysts. Raw materials include algae (Chow et al., 2013; Duan et al., 2013), crop residue (Liu et al., 2013; Zhang et al., 2012), and wood (Cheng et al., 2010; Rivas et al., 2013; Tekin and Karagoz, 2013).

Other studies (D’Souza and Yan, 2013; Zou et al., 2009) have reported that a series of reactions mainly occurred during the liquefaction process, including decomposition, esterification, and polycondensation. The liquefied wood contains depolymerized products from the β1–4 glucosidic bond cleavage of the cellulose and hemicelluloses molecules as well as from low molar mass oligomers. The complex structure of the lignin molecule can be broken into smaller fragments. However, the associated reaction pathways and products have yet to be defined completely.

The liquefaction of wood and other lignocellulosic materials with organic solvents, such as phenols and polyhydric alcohols, is a unique thermochemical conversion process among the biomass applications because this process combines
the useful, functional groups of the biomass and organic solvent to obtain a large variety of biopolymers (Pan, 2011). This process has been studied extensively by several groups. These biopolymer products include coatings (Budija et al., 2009), carbon fibers (Xiaojun and Guangjie, 2010), foams (Alma and Shiraishi, 1998), and adhesives (Alma and Bastürk, 2001; Fu et al., 2006; Kobayashi et al., 2000). The liquefied wood can be used as part of the adhesive mixture because of the presence of free hydroxyl groups, which can polymerize with different functional groups to produce various polymers or to self-crosslink (Budija et al., 2009). The liquefied wood adhesives can also be combined with a mixture of synthetic adhesives or with other natural materials, such as tannins (Cuk et al., 2011).

Lignin has also been used for the production of polyol compounds through the liquefaction process, which can be employed in the preparation of various types of resins.

1.6 Additives

The introduction of a second component to polymers has been accepted; this component is often used to modify the characteristics of the products and to acquire new polymer materials with improved properties. Composite materials have a pivotal role in industries that are now considered the most progressive worldwide. Generally, the term “composite” is given to materials made of more than one component. Polymer composites are a mixture of polymers with inorganic or organic additives that have certain geometric forms (spheres, flakes, fibers, and particulates). A wide range of polymer characteristics can be improved by composite technologies, such as their mechanical, thermal, durability, chemical stability, barrier, flame retardance,
corrosion resistance, biodegradability, magnetic, optical, and electrical properties (Armentano et al., 2010; Cosoli et al., 2008; Ma et al., 2006; Pandey et al., 2005).

Fillers are substances that can be added to various polymer systems to reduce the cost or improve their properties (Giannelis, 1998; Pavlidou and Papaspyrides, 2008). This material can be added as a solid, liquid, or gas. For example, the use of a minimal percentage of clay loading can lead to significant improvements in the mechanical and thermal properties (Giannelis, 1998; Pavlidou and Papaspyrides, 2008). In general, the fillers used to modify the properties of polymers can be classified into two categories: inert fillers and active fillers. Inert fillers come from inorganic mineral powders, such as kaolin, diammonium phosphate, porcelain clay (which is frequently used), sodium silicate, and magnesium oxide. These fillers are used to reduce cost. These mostly hydrophilic materials can be dispersed in adhesives. Active fillers are organic compounds, which swell when dissolved in a solution. These fillers include the cellulose-type fillers (wood powder, bark powder, etc.), protein-type fillers (soy protein, blood powder, etc.), and starch-type fillers (wheat flour, etc.). These materials have the ability to react with resins.

Clays are one group of additives that have been widely used in the preparation of polymeric composite materials. Recently, increasing attention has been given to the development of polymer/clay nanocomposites because of their dramatically improved properties as compared with conventional fillers after the addition of very low portions of the filler (Thostenson et al., 2005). Clay minerals are used in soil science and sedimentology to refer to particles formed by the combination of tetrahedral and octahedral aluminosilicate ([SiO₄]⁻⁴ and [AlO₄]⁻⁵) layers that are 1 nm thick with 200–300 nm lateral dimensions, as shown in Figure
Clay minerals are important materials that are mainly hydrated aluminosilicates with neutral or negative charges (Murray, 2000). The internal and external cations can be changed by inorganic or organic cations (Alexandre and Dubois, 2000; Lebaron et al., 1999).

The hydrophilic nature of clays makes them poorly suited for mixing with most hydrophobic polymer materials. In addition, the poor physical interaction between the organic components in polymeric materials and the inorganic components in clay leads to their separation and the formation of discrete phases. Therefore their mixtures have poor properties, and this incompatibility prevents the dispersion of clay layers within polymer matrix, thereby leading to weak interfacial interactions (Giannelis, 1996; Singla et al., 2012; Van Olphen, 1977). Moreover, electrostatic forces tightly link the clay platelets with each other. Only some hydrophilic polymers are miscible with layers of clay; these materials are used in the preparation of polymer–clay composites such as poly(vinyl alcohol) and poly(ethylene oxide) (Pavlidou & Papaspyrides 2008).
For these reasons, clay requires pretreatment before it is used as filler in polymer composites. These piles of clay platelets have dimensions much larger than one nanometer. Therefore, untreated clay would be ineffective during use because most of the clay would be trapped inside and unable to react with the polymer matrix. Generally, the intercalation of clay with different organic species is the basic condition for compatible composite materials to ensure the interaction between the clay surfaces and the polymeric components. The intercalation or surface modifications decrease the surface energy of clay layers and match their surface polarity with polymer polarity. The low surface energy of organoclays is more compatible with organic polymers and can intercalate with the interlayer space under specific experimental conditions.

This spacing of organoclays is affected by a variety of factors, including the chemical structure of the surfactant, the degree of cation exchange, and the silicate layer thickness (Maiti et al., 2002). Organically modified clays have been extensively studied in various practical applications in the field of organic-inorganic hybrids, composites, and nanoscale composites (Singla et al., 2012). The surface modification of clay layers can be performed through an ion exchange process via the replacement of cations, such as sodium and calcium, in the interlayer space by ammonium or phosphonium surfactants, which usually include benzyl groups and short aliphatic chains (Ahmad et al., 2009). In addition to modifying the surface and increasing the hydrophobicity of clay layers, the introduction of alkylphosphonium (R₄P⁺X⁻) and alkylammonium (R₄N⁺X⁻) cations into the clay layers increases the distances and spacing of the clay layers, which facilitates the intercalation of the polymer chain during the preparation of nanocomposites (Chigwada et al., 2006). Moreover, the
cations ($R_4N^+X^-$) and ($R_4P^+X^-$) can provide the necessary functional groups that have the ability to interact with the polymer chains or to initiate polymerization processes, thereby increasing the interfacial interactions, as shown in Figure 1.9.

![Figure 1.9: Scheme of the modification of clay layers by organic onium cations (Olad, 2011)](image)

1.7 **Problem statement**

Wood adhesives have a very important role in the industry of wood-based panels. The performance of wood panels eventually depends on the significant efficiency of the adhesive. Synthetic condensation resins based on formaldehyde have been widely used; these resins include urea formaldehyde (UF), phenol formaldehyde (PF), resorcinol formaldehyde (RF), and melamine formaldehyde (MF). The source of all the components of these adhesives is derived from fossil oil. The PF resin is drastically used as a wood adhesive and is also used in boards for use under exterior weather conditions, such as weatherproof plywood, oriented strand
boards (OSB), medium density fiber boards (MDF), or particle boards. The phenol and formaldehyde used to prepare PF resin are toxic materials and contribute to CO\textsubscript{2} emissions, thereby influencing climate changes. Both materials are non-renewable and toxic. In addition, the World Health Organization’s International Agency for Research on Cancer (IARC; an advisory board to the World Health Organization) in 2004 reclassified formaldehyde from group 2A (probably carcinogenic to humans) to group 1 (carcinogenic to humans). This reclassification was primarily based on the results of a National Cancer Institute (NCI) study of workers with occupational exposure to formaldehyde. These results indicated that formaldehyde causes nasopharyngeal cancer (NPC) and is associated with leukemia. However, an outright ban on the use of formaldehyde in wood-based products is currently unlikely because the industry is dependent on the current efficient technologies.

Certainly, formaldehyde is evidently liberated during the production and use of composites of wood bonded with formaldehyde-based adhesives. This formaldehyde emission primarily comes from the remaining free formaldehyde in the adhesives as well as the hydrolysis of adhesives.

Malaysia has more than 4 million hectares of oil palm plantations that yield an estimated amount of 90 million tons of renewable biomass (front, trunk, palm press fiber, shell, and empty fruit bunches), which is generated from the mechanical processes of palm oil production (Malaysia Palm Oil Board, 2013). Unfortunately, oil palm biomass is still treated as a waste without considering the value of their components, such as cellulose, hemicelluloses, and lignin (Mohamad Ibrahim et al., 2006). The biomass remnants must be eliminated in a systematic and scientific manner because the presence of such residues is a danger to the environment.
However, the rapid development of human society, concerns on the fossil fuel shortage, pollution, and end-of-life disposal issues are attracting the most attention nowadays. Therefore, more efforts from governments, industries, and research institutes have been paid to the sustainable development than it has ever been done before for the reduction or replacement of synthetic adhesives for wood panels to decrease the emission of formaldehyde. Cellulose, lignin and hemicellulose are the major components of biomass and the most abundant biopolymers in nature.

1.8 Objectives

The recovered lignin from oil palm (*Elaeis guineensis*) empty fruit bunches (OPEFB) can be incorporated in the preparation of environment friendly wood adhesives. The project was implemented to achieve the following objectives:

1. To extract and to characterize lignin from oil palm (*E. guineensis*) empty fruit bunches via direct pulping processes.
2. To modify the lignin and prepare lignin polyols via: (a) the liquefaction of lignin by a mixture of polyethylene glycol (PEG 400) and glycerol, (b) the liquefaction of lignin by propylene oxide, and (c) the liquefaction of OPEFB.
3. To modify the tannin using oligomer precursors of poly(amine-ester) and prepare lignin/tannin-based wood adhesives.
4. To characterise environment friendly wood adhesives based on lignin polyols incorporated with tannin adhesives and liquefaction of OPEFB fiber as an adhesives.
5. To study the influence of polyethylenimine (PEI) and two kinds of bentonite clay, namely, inorganic and organic bentonite clays on the physical and mechanical properties of wood adhesives based on lignin polyols prepared from liquefaction of OPEFB.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Wood adhesives now represent a vital aspect of the wood-based panel industry, and synthetic condensation resins have become widely used. The synthetic resins used can be classified into four varieties, and all these adhesives are based on formaldehyde. These resins are urea formaldehyde (UF), phenol formaldehyde (PF), resorcinol formaldehyde (RF), and melamine formaldehyde (MF). The PF resin is used in wood adhesives, thermal insulation materials, coatings, molding compounds, and other applications. The high stability of the C-C linkages between the aromatic ring and methylene bridge as well as the resistance to hydrolysis make it a favorite resin for glue lines as well as boards, such as weatherproof plywood, oriented strand boards (OSB), medium-density fiber boards (MDF), or particle boards for use under exterior weather conditions. The global demand for PF resin (resol, novolac, and others) continues to increase; recent reports expect this demands to grow at an annual rate of 5.7% from 2014 to 2019 by $19.31 billion. This increased demand is associated with the increased construction in developing regions (Transparency, 2013). The resol phenolic resin accounted for more than 75% of the global market in 2013. This market is expected to grow at a healthy rate of 4.1% until 2019 (Transparency, 2013). The PF resin is obtained via condensation reactions between phenol and formaldehyde in the presence of an acid or a base to produce novolac or resol, respectively. Resol type PF resins (Scheme 2.1) have been widely used for decades to manufacture wood adhesives because of their high performance in terms of the mechanical and thermal properties as well as its water resistance.
Scheme 2.1: Synthesis of phenol-formaldehyde resins by polycondensation of phenols, in excess of formaldehyde developed by Baekeland (1909)

Concern regarding crude oil supplies and the toxicity of the raw materials extracted from the fossil fuels has grown because they can cause climate change. According to findings conducted by the National Cancer Institute (NCI) on a group of workers who were exposed continuously to formaldehyde, high possibility of cancer was diagnosed, prompting the World Health Organization to the reclassification of formaldehyde to group I. Wood-based panels industry relies heavily on this material, making it difficult to impose an outright ban on the use of formaldehyde.

Recently, the development of natural or green-based wood adhesives as successful substitutes for synthetic resins has become of interest because of the unwarranted increase in the prices of fossil fuels as well as environmental and health concerns. Lignin and tannin are materials rich in phenolic compounds; both were found to be successful alternatives for phenol in the manufacturing of bio-based PF resins.
2.2 Lignin-based wood adhesives

Lignins are amorphous three-dimensional network polymers that exist in all vascular plants. These materials are obtained as a byproduct of the wood pulping process. As reviewed by (Pye, 2006), lignin can be regarded as a raw material for various applications. The opportunities and challenges of the use of lignin were described in an extensive study (Gosselink, 2011). Their report showed the importance of lignin in the multiple applications. The potential uses of lignin can be classified into different groups: (1) power-fuel-syngas, (2) macromolecules, and (3) aromatics. The second group benefits from the structure of lignin; these applications require lignin with high molecular mass, such as wood adhesives (binders), polyurethane foams, and carbon fibers (Gandini and Belgacem, 2008).

Given the chemical and structural similarity between PF resin and lignin (Figure 2.1) the mixture of these synthetic resins have received much interest. In addition, their auto-adhesion has been used, wherein lignin is activated via methods such as treatment with Fenton’s reagent, enzymatic activation, exposure to γ-radiation, and steam explosion (Hemmilä et al., 2013; Van Langenberg et al., 2010).

Figure 2.1: Comparison between partial PF resin and lignin structures
The polymerization reactions that can increase the lignin concentration in wood adhesives should be understood, and thus the structure and chemical composition of lignin should be studied. As previously mentioned, the natural form of lignin is a three-dimensional polymer that is broken into smaller segments by the pulping processes.

The chemical features of the lignin structure can be utilized for polymerization reactions of wood adhesives. These features are:

1. Phenolic hydroxyl groups,
2. Aliphatic hydroxyl groups,
3. Structures that can form intermediates of quinone methide,
4. Effective unsubstituted 3- or 5- sites in the phenylpropanoid units.

![Lignin structure with effective unsubstituted 3- or 5- sites](image)

Figure 2.2: Lignin structure with effective unsubstituted 3- or 5- sites

The cross-linking reaction can occur in the lignin through condensation or free radical coupling reactions. The condensation reaction using heat and mineral acids in lignin is not as effective as in PF resins because of the low number of reactive sites in the aromatic ring of lignin (Dunky, 2003) as well as their much
lower reactivity towards aldehydes or formaldehyde as compared with phenolic resins. First, only 0.5 of a free 5-position (ortho to the phenolic groups) per phenylpropyl (C9) unit is available; positions 2 and 6 are less reactive. Second, less than one benzyl alcohol or ether group is present per C9 unit in lignin, whereas up to three methylol groups can be introduced into one phenolic ring in synthetic PF resins. Finally, the complexity of the lignin structure and the aromatics leads to its considerably less reactivity toward hydroxybenzyl alcohol groups than phenol. The presence of methoxy groups adjacent to the phenolic hydroxyl groups causes steric hindrance on the reaction of formaldehyde and the formation of methylene bridges. All of these reasons lead to disadvantages, including the rate of the curing process. Therefore, the press temperatures are higher and the time required for the press would be longer than those required by synthetic resins. These conditions are actually unacceptable in practical applications. Moreover, lignin has the ability to cross-link with itself in the presence of hydrogen peroxide, sulfuric acid, or specific enzymes. Research on the use of lignin-based wood adhesives dates back to more than 100 years (Dunky, 2003; Effendi et al., 2008; Hamarneh, 2010; Pizzi, 2006). However, this feature severely limits its use in industrial applications. Among the industrial applications, none of these applications relied on the use of pure lignin without the addition of synthetic resins or the modification of the lignin structure were successful (Dunky, 2003; Effendi et al., 2008; Hamarneh, 2010; Pizzi, 2006). Some of the recently used methods rely on thermal conversion for the production of pyrolytic lignins, such as vacuum pyrolysis, fast pyrolysis, pressure liquefaction, and phenolysis. These raw materials are of interest for the production of biomass at a low cost as well as their easy incorporation with phenolic resins (Effendi et al., 2008).
A large number of patents have been submitted in the past four decades that deal with lignin as adhesives for plywood, particle boards, and fiber boards in the absence of traditional PF and UF resins (Nimz, 1983). Aside from lignin, the addition of cross-linking agents is necessary in most cases; these agents include polyacrylamides, epoxides, polyols, polyisocyanates, polyethyleneimines, aldehydes, proteins, and so on. Most of these procedures have not been used in large-scale practical applications for different reasons. Very few procedures, such as those of Pedersen and Jul-Rasmussen (1963), Pelikan et al. (1954), Pedersen and Jul-Rasmussen (1963), Shen (1973), Nimz et al. (1972), use lignosulfonates or spent sulfite liquor (SSL) without cross-linking chemicals (Nimz, 1983). In principle, lignin can be applied as an adhesive material via the Pedersen process, which need long press times because of the low reactivity of lignin (Nimz, 1983; Pedersen and Jul-Rasmussen, 1962). In the Pederson process, lignosulfonates were treated with strong mineral acids at high temperatures of up to 180 °C. The problem with this process is that condensation took place under strong acidic conditions, which led to significant corrosion problems in the factory (Pedersen et al., 1962). Some of the disadvantages of the abovementioned method (use of strong acids, long press times, and high press temperatures) in the condensation process (Nimz and Hitze, 1980; Nimz, 1983) can be avoided via oxidation of the phenolic ring by hydrogen peroxide with sulfur dioxide as the catalyst (Nimz & Hitze, 1980). This process will form phenoxy radicals, which can associate with each other to form inter- and intramolecular C–C bonds. The oxidation reaction does not require heating or the utilization of strong acidic conditions. Consequently, the process was conducted at a temperature of 70 °C and a lower pH. Pelikan et al. (1954) used chromium trioxide as a cross-linking reagent with lignin to prepare the adhesive for floor layers via
oxidation. The mechanism of the cross-linking reaction is the same as with H$_2$O$_2$ (Nimz, 1983). However, oxidation with CrO$_3$ was much less effective. It was applied to the particleboards, but the result had a low tensile strength and the boards were delaminated in water after less than two hours and at a temperature of 20 °C.

The oxidation of lignin can also be achieved by biochemical methods, such as the addition of enzymes (phenoloxidase laccase) to SSL. Polymerization processes can be initiated via free radicals as shown in Scheme 2.2 (Ghaffar and Fan, 2014). The enzymes that are added were obtained from nutrient solutions of white fungi. The oxidation reaction method of cross-linking has an advantage over condensation reactions because it does not need mineral acids or high temperatures. The recombination of free radicals as well as the formation of C-C and C-O bonds between radicals is a very rapid reaction. Therefore, the reaction requires a very low activation energy (Pizzi, 2003a).

Scheme 2.2: Cross-linking of lignin by oxidative coupling (Ghaffar and Fan, 2014)
Given the research and studies described above, it was inferred that the enhancement of lignin reactivity to an acceptable level is appropriate for the stringent requirements of the press rate and temperature of the panels in the industrial manufacturing processes. Therefore, the lignin structure must be modified (Pizzi, 2006). With the widespread use of lignin in phenolic resin systems, different chemical modifications were performed to evaluate and to improve the effectiveness and compatibility of lignin in PF resin. The main methods in this process comprise demethylation (Schroeder et al., 1990; Wu and Zhan, 2001), methylation (Vázquez et al. 1997; Khan et al. 2004a; Khan et al. 2004b), phenolation (Alonso et al., 2005; Çetin and Özmen, 2002; Lee et al., 2002; Liu et al., 2007), and methylation or hydroxymethylation (Ružinská, 2003; Truter et al., 1994; Zoumpoulakis and Simitzis, 2001). Truter et al. (1994) displayed in detail the cross-linking reaction chemistry of formaldehyde with lignin. Similarly, lignin reacts mainly with formaldehyde under alkali conditions in unsubstituted 5-sites and the formation of hydroxymethylated species (Scheme 2.3). Subsequently, methylene bridges can be formed by reacting these species with phenol or other lignin units to form resins. Given the low reactivity of lignin towards formaldehyde as compared with phenol, the establishment of methylol groups requires much longer reaction periods.

![Scheme 2.3: Polymerization of lignin with formaldehyde in alkaline solution (Truter et al., 1994)](image-url)
To avoid formaldehyde, Gosselink (2011) used metaperiodate as the modification agent to substitute for formaldehyde and to improve the effectiveness of Kraft and soda lignin. The oxidation of lignin with sodium periodate could lead to the formation of carboxyl and carbonyl groups. However, demethoxylation by the Malaprade reaction liberates methanol and forms the ortho and para quinone methides (Adler and Hernestam, 1955). Scheme 2.4 shows the proposed mechanism, which represents the Malaprade reaction for a model of the lignin compound guaiacol.

Scheme 2.4: Proposed mechanism of periodate oxidation of guaiacol via the Malaprade reaction (Gosselink, 2011)

The abundance of lignin with different types of product remnants in pulp mills makes it a promising and interesting material for the preparation of wood adhesives. Previous studies extensively reviewed the use of lignin in the wood adhesives (Feldman, 2002; Pecina and Kuchne, 1995; Roffael and Dix, 1991). The most abundant of lignin type is Kraft lignin, which contains 0.3 active positions per C9 unit. However, some difficulty was experienced in forming acceptable
polymerized products by incorporating PF resins or by other means. This difficulty arises from the presence of unfractionated lignins with a large proportion of low-molecular-weight fragments. Forss & Fuhrmann (1976) used lignin with a molecular weight of less than (5000) in ultrafiltration and formed a phenolic resin with 40 to 70% lignin. The use of these resins depends on the type of application.

Crude lignin is condensation limited, and only allows approximately 20% of lignin to replace phenol in PF resins. When adding more than 20%, the lignin acted as a filler and decreased the characteristics of panels manufactured with wood adhesives (Hse and Hong, 1989; Vazquez et al., 1995; Vázquez et al., 1997). There are higher percentages of the phenol replacement with lignin in the case of chemically enhancing the lignin structure, as referred to above. Replacing 50% of phenol in PF resins by phenolated-lignin could lead to bond strength in the lignin-PF resin becoming similar or better as compared with conventional PF resins (Khan et al., 2004; Mozaffar et al., 2004; Nihat and Nilgu, 2002).

Lignosulfonate extracted from grasses such as wheat straw and bagasse have been used to synthesize PF wood adhesives (Akhtar et al., 2011; Liu et al., 2006). Wood adhesives prepared via incorporation of soda and wheat straw-lignin were placed into phenol-formaldehyde resins for the lower molecular weight fragments (Liu et al., 2008). Peng & Riedl (1994) proved the increase in the effectiveness of lignosulfonate with formaldehyde when adding wheat starch as a filler, producing the lowest level of the condensation reaction.

In 2002, the possibility of replacing the 20 to 30% of organosolv lignin to substitute phenol in synthetic phenolic resins for the production of particleboard without any adverse effects on bonding properties was investigated (Çetin and
Özmen, 2002a, 2002b). Ethanol residue (ER) was produced as the by-product from the extraction of lignin via ethanol pulping, to partially replace phenol in the range of 10-70% to synthesize lignin-PF (LPF). The results showed that ER with lower molecular weight and less methoxy groups as well as less hydroxyl groups are suitable for the preparation of LPF (Zhang et al., 2013).

In another study, Kraft lignin was extracted from OPEFB through Kraft pulping and exhibited significant potential as partial replacement of phenol in phenolic resin production (Mohamad Ibrahim et al., 2011). EL Mansouri & Salvadó (2006) used UV-spectroscopy and Mannich reactivity to show that the soda and the Kraft-anthraquinone lignin were effective towards modification and therefore were good feedstock for the preparation of LPF. Meanwhile enzymatic hydrolysis lignin (EHL) was recovered from residues of cornstalk and was used to modify synthetic PF resin. The bonding strength satisfied the requirements of the Chinese National Standard (GB/T 14732-2006) (Jin et al., 2010).

2.3 Tannin-based wood adhesives

Tannins are natural polyhydroxyphenolic compounds, which contain materials that are extracted from wood, leaves, and fruits. Their phenolic nature makes them as potential adhesives and good alternatives for all or part of the phenol used in wood adhesives. In 1970, the oil crisis and rising prices accompanied by the reduced availability of synthetic phenolic substances stimulated the applied research on the use of condensed tannin as a source of phenol for the production of adhesives. However, synthetic resins became cheaper in 1974 because of the restored availability of oil supplies. After 2000, much interest has been given to renewable
resources, especially tannin. Two main factors led to the growing attention of tannin as adhesives. (i) The prices of synthetic resins disproportionately increased with the market price; thus, raw materials based on renewable resources were preferred. Consequently, tannin became much cheaper than phenol and competes with the cheapest adhesive. (ii) The tightened regulation of formaldehyde emissions through the introduction of the extremely strict Japanese standards, has begun to spread to other countries (CARB, 2006; Japanese Standards Association, 1994).

The first introduced application and the successful marketing of tannin adhesives occurred in the early 1970s in South Africa. To date, synthetic resins for plywood and particle board are no longer used in that country; only mimosa tannin adhesives are used for interior or exterior board applications (Dunky and Pizzi, 2002).

Tannin is subjected to the same well-known reaction of phenol with formaldehyde under acidic or basic conditions; the reactions that depend on weakly basic catalysts are often used in industrial applications. However, the rate of this reaction for the hydrolysable tannins is low; formaldehyde or other electrophilic compounds are required for the formation of the network (Conner, 2001; Pizzi, 2003a; Pizzi, 2006). Therefore, hydrolysable tannin is not preferred in the preparation of wood adhesives. Nevertheless, condensed tannins have been successfully used as alternatives to partial phenol (up to 50%) for the manufacturing of PF resin.

Tannin reacts with formaldehyde to produce polymers with methylene bridge linkages. Effective nucleophilic sites on the A aromatic ring (Figure 2.2) in the
condensed tannins tend to be more effective in substitution reactions than those found on the B ring (Pizzi, 1980; Pizzi, 1983).

Figure 2.3: Effective sites on the A ring in the condensed tannins (Pizzi, 1983)

Tannin compounds can be used as wood adhesives alone (with formaldehyde as a cross-linker) or in combination with phenolic resins or aminoplastics. Valenzuela et al. (2012) studied the utilization of pine tannin extracts, which can be used to obtain the best formulation of wood adhesives in the presence of phloroglucinolic tannins without the need to adjust the pH and with paraformaldehyde or hexamine as a curing agent. The results obtained with the manufactured particle boards were relatively good. The tannin-based wood adhesive was mixed with 4,4'-diphenylmethane diisocyanate (commercial pMDI) at rates ranging from 0 to 30%; the strength of the dry internal bonds increased with the increased proportion of pMDI (Valenzuela et al., 2012). Previous studies have suggested that a combination of renewable resources, such as tannin-furan systems in the formulation of wood adhesives, may be an approach that would make the forest products industry more self-sufficient (Garcia and Pizzi, 1998; Lei et al., 2008). The preparation of wood adhesives is similar to that of marine adhesive proteins (MAP); the mixing of condensed tannins with polyethylenimine (PEI) is possible, wherein
tannin-PEI exhibited high water resistance and high shear strength as a formaldehyde-free system. Unfortunately, this material had a significant loss of bond strength when stored for a long period of time (Geng, et al., 2004; Huang, 2007).

Silva et al. (2012) evaluated the quality of plywood panels manufactured via the replacement of more than 20% of the PF resin by tannin adhesives recovered from the bark of *Pinus oocarpa*. The results showed that the mechanical properties related to the static bending of the MORs parallel and perpendicular to the grain of the panels at this ratio remained unchanged. Their study suggested that in order to achieve higher values of the physical properties of plywood panels, the addition of paraffin is advisable.

Plywood panel production is also possible through the use of *barbatimão* tannin adhesives without any PF adhesives. Carvalho et al. (2014) studied the technical feasibility of mixing different percentages (0%, 25%, 50%, and 100%) of *barbatimão* tannin with commercial PF resin and practically demonstrated that it can be used alone in plywood production under humid and dry environments.

A disadvantage of tannin polyphenols in industrial applications as an adhesive is their high viscosity, which makes the glue mix flow difficult; this property may be attributed to the high molecular weight of tannins and polymeric carbohydrates (Pizzi, 1978; Yazaki and Hillis, 1980). This property leads to the deformation of the wood components (Jost and Sernek, 2009). On the other hand, the high reactivity of the aromatic A ring also has negative side effects, such as the short pot-life and the higher viscosity in the adhesive formulation. The dilution solution method is used to reduce the viscosity by generating steam in the hot pressing of the composite (Rowell, 2012).
Under many conditions used in the formulation of wood adhesives, contrary to popular belief, hexamethylenetetramine (hexamine) is used as a fast-reacting hardener that results in extremely low formaldehyde emissions (Pizzi, 1994). $^{13}$C-NMR spectroscopy has confirmed that the main decomposition of hexamine in these circumstances is not directly related to formaldehyde, but instead consists of intermediate compounds like imines and iminoaminomethylene bases. $^{13}$C-NMR also confirmed the presence of some chemical species with very effective nucleophilic sites, such as resorcinol, melamine, and condensed flavonoid tannins. Hexamine does not decompose to ammonia and formaldehyde, but instead forms intermediate fragments that very effectively react with melamine and tannin, among others, to form aminomethylene bridges before producing formaldehyde (Kamoun and Pizzi, 2000; Kamoun et al., 2003).

2.4 Liquefaction of wood based adhesives

Materials based on biomass, particularly wood, are among the most abundant renewable resources. Recently, significant attention has been given to the preparation of eco-friendly polymeric products from the liquefaction of biomass materials and their derivatives.

The use of phenol and polyhydroxy alcohols in the liquefaction of wood and other lignocellulosic materials, such as lignin, has been studied by several groups (Alma et al., 1998; Hassan and Shukry, 2008; Lin et al., 1994; Yamazaki et al., 2006). Often, the liquefaction process is performed at elevated temperatures and in the presence of acids as catalysts. Various categories of resins were prepared from liquefied biomass, which included phenolics, epoxides, and polyurethane, among
others. The methods of preparation and applications on adhesives, films, and so on have also been discussed.

Given the presence of large amounts of alcoholic hydroxyl groups and phenolics, liquefied wood is highly efficient for the different reactions. The amount of these functional groups depends on the length of the liquefaction process as well as the ratio between the wood content and liquefying solvents. The importance of these factors lies in its possible application to create polyurethane foams (Kurimoto et al., 2001, 2000; Wei et al., 2004). Tohmura et al. (2005) has recently developed wood adhesives from polyalcohol urethane. In addition, epoxy functionality could be introduced through the reaction of hydroxyl groups in the liquefied wood with epichlorohydrin (Kobayashi et al., 2000; Kobayashi et al., 2001). Meal hardwood extracted from Japanese cedar can be used for the preparation of epoxy compounds. Kishi et al. (2006) synthesized epoxy resin-based wood adhesives. Amino compounds can be used as curing agents with epoxy resins. Both systems have been used for the production of plywood, which were obtained with good mechanical and physical properties.

With regard to phenolic resins, thermoplastic and thermoset systems (novolac and resol) can be prepared from biomass liquefaction. The novolac type of thermoplastic phenolic resin was prepared by phenol and formaldehyde reactions with molar ratio more than one under acidic medium. Therefore, the use of an acid as a catalyst in the liquefaction of biomass to reduce reaction temperatures substantially is considered favorable for the synthesis of novolac. Several groups have studied two different types of synthetic techniques for the production of novolac resins based on liquefied biomass. The first type uses directly liquefied wood produced by phenol-
like novolac resins and the other type uses liquefied biomass with formaldehyde for further condensation after liquefaction. Lin et al. (1994, 1995) used phosphoric acid as a catalyst in wood liquefaction to prepare the novolac resin and studied its mechanical and thermal properties. Several factors were found to affect the amount of phenol during the liquefaction process, wherein the reacted phenol increased with the increased liquefaction time, temperature, catalyst amount, and wood-to-phenol ratio. The results showed that the hydrophilicity of liquefied wood with higher amounts of reacted phenol was less than those with lower amounts of reacted phenol. In addition, scanning electronic microscopy showed that liquefied wood-based novolac resins exhibited better compatibility with wood components than commercial novolac resins.

The preparation of novolac resin by the liquefaction of oil palm empty fruit bunch (OPEFB) in phenol was performed with H₂SO₄ as a catalyst. The results showed that when the reaction temperature and catalyst concentration were increased from 110 to 150 °C and from 3 to 8%, respectively, the reaction yield would be increased. The thermal stability of phenolated OPEFB also increased with increasing catalyst concentration (Ahmadzadeh et al., 2008).

The resol type of phenolic resin is the thermoset resin that is synthesized by phenol and formaldehyde reactions with molar ratios less than one under alkaline conditions. A variety of conditions can be used for the reactions to produce resol resin in terms of the catalyst, the ratio of F/P, and other reaction conditions. However, only a few studies have investigated on liquefied wood-based resol resin. This trend may be attributed to the extra step, wherein the acidic liquefied biomass must be neutralized before resin synthesis. Hydroxyl groups in liquefied biomass and
other lignocellulosics materials can react with different reactive positions in
thermosetting systems (Hassan and Shukry, 2008).

The liquefaction of biomass by phenol to synthesize resol phenolic resin was
studied for the production of particleboards; the bonding strength and comparison
with commercial UF resin have been discussed. The internal bonding strength in the
liquefied biomass based resol resin was lower than commercial UF resins. Therefore,
the resin needs longer time for the hot-press process for the full curing of the core
layers. However, the dimensional stability of the panels are better than those of
commercial UF resins (Hassan et al., 2009). In the synthesis process of resol resin,
the nature and quantity of the catalyst have a significant influence on the molecular
structure and, thus, the application properties would be influenced. The effect of
sodium hydroxide (NaOH) as a catalyst to prepare resol resins from liquefied wood
bark has been studied by Yuan et al. (2009). Different methods were used to prepare
the resin, and these methods depend on the ratio of NaOH added to the liquefied bark
in three steps. The amounts of NaOH added in steps 1 and 2 were fixed at 4.5% and
20.5%, respectively, based on the weight of liquefied bark (solid base). The extra
amount of NaOH added in step 3 varied from 0 to 6%. Their study showed that the
resin prepared with the two-step addition of NaOH had higher viscosity and shorter
shelf-life than those with the extra addition of NaOH. However, the shelf-life of all
types of liquefied bark-based resol resin were lower than that of commercial PF
resins (60 days). Therefore, the liquefied bark-based resol were more reactive toward
formaldehyde than commercial PF resins. In addition, the formaldehyde emissions of
liquefied bark based resol resins were higher than the commercial PF resin but still
within the required relevant national standards of Japan and China.
Wang et al. (2009a, 2009b) investigated the preparation of bio-oil phenolic feedstock from the liquefaction of corn stalk by hot-compressed phenol–water for synthesizing resol resins. The liquefaction was conducted at 300–350 °C and 2.0 MPa under a nitrogen system. This type of liquefaction is classified as hydrothermal conversion, which differs from thermochemical conversion, because water serves as a reaction medium and phenol prevents the degradation of lignin intermediates from the formation of char. The bio-oil fraction was used to synthesize resol type phenolic resin. The bio-oil-based resol resin is characterized by a high molecular weight and a higher polydispersity as compared with the commercial PF resol.

The liquefaction of biomass with 48% of phenol under alkaline conditions for the preparation of all resol and novolac resins has been studied by some researchers to avoid the neutralization of the acid catalysts after liquefaction (Maldas and Shiraishi, 1997; Maldas et al., 1997). The liquefied mixture showed that the amount of non-reacted phenol was much higher than the amount of strong acid used as a catalyst in the liquefaction process.

Lee & Liu (2002) synthesized a resol type of liquefied bark, which was used in particleboard preparation. Similarly, liquefied bamboo was used to prepare a PF adhesive (Shenyuan et al., 2006). In this context, Zhang et al. (2007) used Chinese fir and poplar for liquefaction. The bonding strength of their adhesives in plywood successfully showed their compatibility to international requirements. Bark pyrolysis oils were extracted from softwood and used to prepare adhesives for particleboards using isocyanates as a curing agent (Gagnon et al., 2004). The production of pyrolysis oil from bark residues from paper and pulping processes was also reported.
Different ratios of phenol were substituted to synthesize pyrolysis oil-based resol resins. The resulting mechanical properties of strand boards with these resols were compatible with panels made from commercial resols (Amen-Chen et al., 2002).

Lignin liquefied with phenol in the presence of H2SO4 or HCl catalysts has been used as the raw material for the preparation of resol-type PF resins by reacting with formaldehyde under alkaline conditions. The phenol-liquefied lignin resin exhibited shorter gel time at 135 °C. This resin was used in plywood manufacturing; the tensile strength results in dry, cold, and warm water-soaked conditions that satisfied the CNS 1349 standards (Lee et al., 2012).

Zhao (2013) studied the preparation of bio-based PF resol resins; the liquefied bark of the mountain pine beetle (MPB) was converted via liquefaction by phenol in the presence of acid catalysts and bark alkaline extractives. Their study found that the conversion process effectively replaced phenol with yields of 85 and 68% for the liquefied bark-PF resol resin and bark extractive-PF resol resins, respectively. The resol resin types exhibited higher molecular weights, higher polydispersity, shorter gel times, and faster curing rates than the control PF resin. In addition, the dry and wet bonding strength of bio-based PF resin were comparable with those of commercial PF resin. The thermal stability was likewise similar between the bio-based and commercial PF resins.

Kunaver et al. (2010) used a mixture of diethylene glycol and glycerol to liquefy various types of hardwoods and softwoods. The liquefied spruce wood was subjected to a condensation reaction with different percentages of melamine–urea–formaldehyde and melamine–formaldehyde in the hot press to prepare adhesives for the production of wood particleboards. The determination of formaldehyde emission
and mechanical properties proved that the addition of 50% of the liquefied wood to these resin precursors led to products compatible with the European standard quality requirements for particleboards. A reduction of up to 40% of the formaldehyde emission was also achieved. Poplar wood has been liquefied using different solvents (ethylene glycol and glycerol). The liquefied wood produced by glycerol was mixed with a synthetic PF adhesive in concentrations ranging from 0 to 100%. The curing rate was achieved in a hot press at 180 °C. Meanwhile, liquefied wood from ethylene glycol can be used as an independent adhesive and then mixed with tannin adhesives. The curing rate for specimens was achieved in a hot press at 200 °C. The shear strength of the dry samples increased when 25% of the synthetic PF adhesive was replaced by liquefied wood with glycerol. However, when a higher percentage of liquefied wood was used, the bond shear strength decreased. The bonding strength of specimens with liquefied wood produced by ethylene glycol had higher shear strength than the adhesives made of liquefied wood with glycerol (Ugovsek et al., 2010).

Yanqiao et al. (2013) prepared lignin polyols via the liquefaction of enzymatic hydrolysis lignin (EHL) with a solvent mixture of glycerol and polyethylene glycol 400 with sulfuric acid as a catalyst at 130 °C. The modification of synthetic PF resin was conducted by EHL-polyols. The results showed that most of the properties such as the solid content, phenol content, pH value, formaldehyde emission, and bonding strength met the requirements of the National Standard GB 9846.1-12-88 when 5 to 25% of phenol was replaced by EHL-polyols.
2.5 Modification of wood adhesives using additives

At present, synthetic adhesives based on formaldehyde such as PF, UF, and MF are predominantly used for wood composite production. These adhesives have some advantages and disadvantages. For example, UF adhesives have advantages such as the lack of color in the cured polymer, low price, good mechanical properties, and so on. Consequently, these adhesives are commonly used in the wood panel industry. However, UF resin can only be used as an interior adhesive because of its poor water resistance. The use of PF adhesives is as important as UF adhesives in the wood panel industry. The good water resistance of PF adhesives allows them to be used under more stringent conditions than UF adhesives; thus, PF adhesives can be classified as exterior adhesives. However, their application is still limited because of its brittleness, brown color, high curing temperature, long curing time, and toxicity due to liberation of phenol and formaldehyde (Gu, 1998). A variety of methods have been used to improve the performance of UF and PF adhesives as well as to expand their use. These methods are widely used in the industry; they include the simple addition of fillers. A variety of resin properties can significantly improve their performance as wood adhesives by the addition of fillers, which are most important for their lower cost. The mechanical performance of the resin is also improved in most cases. Moreover, the addition of fillers could reduce shrinkage and alleviate the stress on the glue line, which improves the hardness and durability. The flow of the adhesive and its smooth flow on the wood surface will be improved because of the penetration of water into the glue in the presence of a filler. The moderate permeability of the glue between the wood components has good mechanical effects by physically interlocking the wood surface with the curing agents; thus, the bonding strength between the wood products is improved.
Wheat flour is an activated filler, which is most commonly used in factories for the production of UF resins. The addition of approximately 10 to 20% of the wheat flour to the total solid resin can increase the weather resistance of the resin because this filler can reduce the shrinkage of the glue line (Lei, 2009). According to Ma (1995), the use of oxidized starch as a filler with UF resin at proportions of 5–10% will decrease the free-formaldehyde emission from 3–7% to 0.2–0.5%. The hydroxyl group reacts with starch molecule chains and liberates formaldehyde to form acetal, thereby reducing the free formaldehyde emission. Compared with wheat flour, oxidized starch as a filler can further increase the bonding strength and water resistance of UF resins (Shi, 2003).

Mosiewicki et al. (2004) studied the mechanical and thermal behavior of a composite formulated from a natural quebracho tannin adhesive with pine wood flour as well as the effect of moisture on its adhesive properties. The results showed that the mechanical and thermal properties of composite materials of wood flour/tannin adhesives have sufficient values for use in some industrial applications in terms of its higher stiffness, which is an important requirement. However, this composite material can be used in the dried state alone and must be avoided in humid atmospheres.

Kargarfard & Jahan-Latibari (2012) used recycled polyethylene with UF to reduce swelling fish and water absorption during particleboard production, thereby improving its performance in terms of weather resistance. In this work, different amounts of recycled polyethylene (5%, 10%, and 15%) were mixed with the lowest amount of UF resin (4%). Their results revealed that 5% of recycled polyethylene in the surface layer could improve the weather resistance of particleboards. The
modulus of rupture (MOR) and modulus of elasticity (MOE) properties were marginally increased when the percentage of recycled polyethylene was increased to 5% in the surface layer. However, when 15% recycled polyethylene was added to the surface layer, the increased MOR was almost doubled and the MOE was increased by approximately 50% as compared with the control boards.

Du et al. (1995) used the synergistic effect of mineral filler (MgO and SiO$_2$) with UF adhesives for the production of plywood. Plywood has better performance with mineral fillers as compared with the absence of filler or with wheat flour fillers. These results can be attributed to two reasons. (i) The (MgO and SiO$_2$) filler prevents the glue from excessive permeation into the wood substrate and reduces the internal stress caused by the shrinkage. (ii) The oxygen from silicate and magnesium may be linked with the hydroxymethyl groups of the UF adhesive thereby improving the durability and weather resistance of the resins.

Another newly developed type of mineral fillers are the nanomaterials, which differ physically and chemically from the normal fillers in terms of their thermal, light, radiation, and mechanical characteristics, among others (Cavicchi and Silsbee, 1984). Polymer nanocomposites have attracted considerable attention from researchers, especially in research related to polymer/layered silicate (PLS). This interest is attributed to the fact that the addition of small amounts of these materials often significantly improves the mechanical and thermal properties of polymers.

Some researchers have tried to use the nanomaterial fillers in wood adhesive systems, such as nano-SiO$_2$, nano-CaCO$_3$, and nano-montmorillonite (MMT) (Lin et al., 2005; G. . Yang et al., 2004; G. D. Yang et al., 2004; Yu et al., 2002). Their results showed that the adhesive bonding strength, gel time, and free formaldehyde
emission were affected by the addition of nanomaterials. In most cases, the emission of free formaldehydes was significantly reduced.

The exfoliated nano-MMT was used by Zhang et al. (2013) as a nanomineral filler with polymeric MDI to modify degraded soybean-protein (DSP) and improve its water resistance and technical applicability. The DSP adhesives with MDI as a crosslinking agent showed improved water resistance and bond strength but their shelf-life is very short. After the modification of MDI/modified DSP by nano-MMT, the produced adhesive had a much longer shelf-life but slightly lower bonding strength.

Various PLSs have been successfully used with various types of resins, such as epoxy (Lan et al., 1995; Lv et al., 2002), polyacrylic ester (Dong and Lee, 1995), polyurethane (Carsten et al., 1999; Tien et al., 2000), and even PF (Choi et al., 2000). However, research on the feasibility and the mechanism of wood adhesive modification with MMT is rather limited.
CHAPTER 3

METHODOLOGY

The extraction, modification and characterization of lignin have been implemented in the School of Chemical Sciences, Universiti Sains Malaysia (USM) laboratories. Oil palm empty fruit bunch was used to obtain Kraft and organosolv lignins by pulping processes. The characterization of all adhesive samples, which included lignin/tannin, modified lignin/tannin, lignin/modified tannin, liquefied wood/tannin, in addition, the modification of adhesives samples via blending with other polymers (polyethylenimine) or modification by clay fillers have been conducted in various schools in USM.

3.1 Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hydroxide</td>
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</tr>
<tr>
<td>Sodium sulfide</td>
<td>QREC (ASIA)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>QREC (ASIA)</td>
</tr>
<tr>
<td>Polyethylene glycol (PEG 400)</td>
<td>R &amp; M Chemicals, Essex, U.K</td>
</tr>
<tr>
<td>Glycerol</td>
<td>HmbG Chemicals</td>
</tr>
<tr>
<td>Pyridine</td>
<td>Merck-Schuchart</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>Merck-Schuchart</td>
</tr>
<tr>
<td>1, 4-Dioxane</td>
<td>HmbG Chemicals</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>QREC (ASIA)</td>
</tr>
<tr>
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<tr>
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<tr>
<td>Acetic acid</td>
<td>Systerm®</td>
</tr>
</tbody>
</table>
3.2 Materials

The oil palm empty fruit bunch (OPEFB) (*Elaeis guineensis*) long fiber was supplied by local plantation, Malaysia specializing in the recycling of lignocellulose waste. The long fibers of OPEFB were washed with water and left exposed to the sun for 3 days. The air-dried OPEFB was ground (20-60 wire mesh) using a Wiley mill and then was further dried at 50 °C for 24 hours in an oven. Tannin in powder form was supplied by Xian Aladdin Bio-Tech Co., Ltd (China).

All chemical materials used in this work were of reagent grade and were used as received without further purification.

3.3 Preparation of Kraft lignin from oil palm empty fruit bunch

3.3.1 Kraft Pulping

Kraft pulping process (Figure 3.1) was carried out in a 10-L digester. Solutions were prepared by dissolving 190 g of NaOH in 1.5 L distilled water (19% based on raw material) and 250 g of hydrous Na₂S in 1.5 L of distilled water (25% based on raw material), with a solvent-to-fiber ratio of 8:1. The cooking temperature was set from room temperature to 170 °C for 3 h. The contents in the digester were stirred by rotating the digester, which was controlled by a motor. The pressure of Kraft pulping was around 12 to 15 bar. After cooking, the pulp was washed and separated by screening through a sieve and then the black liquor was collected.
3.3.2 Kraft lignin extraction

The Kraft black liquor has a pH of 12.5. Kraft lignin (KL) was precipitated from the concentrated black liquor by acidification using 20% (v/v) sulfuric acid (pH 2) (Mohamad Ibrahim et al., 2011). Precipitated lignin was filtered and washed with distilled water at pH 2 and then dried in a vacuum oven at 45 °C for 48 h (Mohamad Ibrahim et al., 2004). The lignin was purified by extraction in the soxhlet apparatus for 6 h with n-pentane to remove the lipophilic non-lignin matters, such as wax and lipids. This step was followed by filtration and washing of the product using distilled water (normalized at pH=2) to remove the excess amount of n-pentane and non-lignin phenolic compounds that may have remained after the pulping process. The purified KL was dried in a vacuum oven at 45 °C for 48 h. KL was treated with hot water to dissolve the residual sugars (Lin, 1992). Finally, the obtained lignin was again dried in a vacuum oven at 45 °C for 48 h.

![Figure 3.1: Extraction of lignin by Kraft pulping process](image_url)
3.4 Organosolv lignin extraction

In this work, strong acids were not used in the delignification process when preparing organosolv lignin unlike most previous studies that focused on using strong acid as catalysts, which has led to the uneconomically process due to high corrosion of the equipment containing strong acids.

Organosolv lignin (AEL) was recovered as a byproduct from OPEFB using autocatalyzed ethanol–water pulping process as shown in Figure 3.2. The air-dried OPEFB was ground from 20–60 wire mesh using a ball mill. The OPEFB was dried overnight at 105 °C in an oven prior to the pulping process. The mass ratio between dried OPEFB and the used solvent was 1:10. The 0.5 L stainless steel reactor was loaded with the raw material (22 g) and 80% aqueous ethanol, and then heated to the operating temperature up to 210 °C for 2 h (cooking process). The reaction mixture was heated at a rate of 5 °C min⁻¹ with continuous stirring. After cooking, the reactor was quenched rapidly to room temperature in an ice-water bath to terminate the reaction. The solid and solvent fractions were separated using a filter paper and washed with warm (60 °C) aqueous ethanol (8:2, 3x 50 ml). The filtrates and original liquid fractions were combined and poured in distilled water with continuous stirring for 30 min to precipitate organosolv lignin. AEL was then collected by centrifugation at 3500 rpm for 15 min. AEL was obtained by freeze-drying for further analysis.
3.5 Preparation of lignin/tannin resin

3.5.1 Preparation of glyoxalated lignin resin

The glyoxalated process of lignins was conducted according to the procedure by El Mansouri et al. (2011) as follows: The lignin powder (29.5 parts by mass) was
gradually added to 38.4 parts of water while the NaOH solution (30%) was added periodically to maintain the pH of the solution between 12 and 12.5 for better dissolution of the lignin powder, which was also facilitated by a vigorous stirring with an overhead stirrer. This mixture was placed in a 250 mL flat bottom flask equipped with a condenser, thermometer and magnetic stirring bar and heated to 60 °C. A quantity of 17.5 parts by mass of glyoxal (40 wt% in water), were added and the lignin solution was maintained at pH of 12-12.5, with a magnetic stirrer on a hot plate for 8 hours.

3.5.2 Preparation of tannin resin

Tannin solution was prepared with 45% (w/v) concentration and its pH was adjusted to 10 with 33 % (w/v) NaOH solution. 6% (w/w) of hexamine (based on tannin) was added to form 33% (w/v) solution as a hardener.

3.5.3 Blending adhesives lignin/tannin

The adhesive tannin glyoxalated lignin (TGL) (final resin) was composed by blending tannin solution with the glyoxalated lignin in a 60/40 solids proportion (w/w).

3.6 Preparation of polyols

3.6.1 Polyols by liquefaction of OPEFB with polyhydric alcohols

The air-dried OPEFB was ground (20-60 wire mesh) using a Wiley mill. The OPEFB was dried overnight at 105 °C in a laboratory oven prior to the liquefaction
process. The mass ratio between dried OPEFB and the used solvent was 1:10, in which 3% of the sulfuric acid (based on the solvent content) was added. Then, 30 g of dried OPEFB was placed in a round-bottom flask equipped with the mechanical stirrer, condenser, and a thermocouple. Thereafter, 9 g of 95% (w/v) aqueous sulfuric acid was added as catalyst together with 300 g of PEG 400 and glycerol (GLY). The flask was immersed in a silicon oil bath and was heated at 160 °C for 4 h. The flask was then cooled to room temperature in an ice-water bath to quench the reaction. Then, 600 mL of 80% (w/v) 1, 4-dioxane aqueous solution was added to the reaction mixture. The resulting mixture was filtered through a filter paper to remove the insoluble parts of the wood. The mixture of 1, 4-dioxane and water was evaporated under reduced pressure after filtration. The mixture was obtained by using a water pump to acquire the liquefied wood, which contains PEG 400 and GLY. The resulting residual was transferred to a three-necked flask equipped with a mechanical stirrer, condenser, and thermocouple. The flask was heated at 140 °C for 2.5 h. The solution was mixed with 2 L of distilled water with continuous stirring for 30 min after the flask was cooled. The viscous lignin polyols were then collected by centrifugation at 3500 rpm for 15 min, and then PEG/GLY-lignin was obtained by freeze-drying.

3.6.2 Polyols by liquefaction of Kraft and organosolv lignins with polyhydric alcohols

The liquefaction process was conducted as proposed by Jin et al. (2011) with slight modifications. PEG 400 and glycerol were used as liquefaction solvent with a weight ratio of 9:1 and with sulfuric acid as catalyst (3% wt. of solvent weight ratio).
Lignin/liquefying reactants were also applied at a ratio of 1:5. PEG 400 is a low molecular weight grade of polyethylene glycol ($M_n = 380-420 \text{ g.mol}^{-1}$). Liquefying reactants were placed into a 250 mL three-necked glass flask immersed in a silicon oil bath and then heated. The flask was equipped with a reflux condenser and thermometer under constant magnetic stirring under nitrogen atmosphere. Lignin was gradually added into the liquefying reactant when the temperature reached 160 °C. The liquefaction reaction was performed for 1 h to obtain a homogeneous liquefied product. The flask was then rapidly cooled in an ice bath to quench the reaction, and the liquefied products were oven dried at 105 °C to constant weight before further analysis.

### 3.6.3 Polyols by liquefaction of Kraft and Organosolv lignins with propylene oxide

Oxypropylation reactions were conducted according to Ahvazi et al. (2011), with slight modifications. Kraft lignin (0.5 g) was dispersed in 250 mL of a 37% (w/w) solution of propylene oxide in water under constant agitation for 30 min. To this mixture, 12.5 mL of 0.1 N NaOH under alkaline conditions was added and allowed to react at room temperature under constant agitation for 7 days. After the reaction was complete, excess propylene oxide was removed under reduced pressure. The product was oven dried at 105 °C to constant weight before further analysis.
3.7 Preparation of wood adhesives by polyols

The same method used for the preparation of lignin/tannin adhesives was adopted for the preparation of lignin polyols/tannin adhesives.

3.8 Preparations of water resistant wood adhesives

3.8.1 Modification of tannin by hyperbranched poly (amine-ester)

3.8.1.1 Preparation of oligomers of the hyperbranched polymer

Hydroxyl-terminated hyperbranched poly (amine-esters) (HBPAE) were synthesized by reacting 1,1,1-trimethylolpropane (as a molecular core) with N,N-diethylol-3-amine methylpropionate (as an AB2 monomer). The HBPAE was prepared as reported elsewhere in the literature (Lu et al., 2000; Zhang et al., 2009). N,N-diethylol-3-amine methylpropionate (AB2) was synthesized via Michael addition. In a three-necked flask equipped with a thermometer, stirrer and reflux condenser, the same mole ratio (0.33 mol) of methyl acrylate and diethanolamine in the presence of methanol was mixed in the flask under nitrogen atmosphere at room temperature for 24 h. Under the reduced pressure, the residual methanol and methyl acrylate were eliminated from the reaction system. The reaction product (AB2) was a colorless transparent oily liquid. Subsequently, through a pseudo one-step process of alcoholysis, 0.1 mol of 1,1,1-trimethylolpropane, 0.3 mol of AB2 and 0.5 wt% of \( p \)-toluene sulfonic acid as a catalyst were stirred at 120 °C for 3 h. The obtained hyperbranched poly (amine-esters) precursor (hydroxyl-terminated) was symbolized as HBPAE. Finally, HBPAE with 5 g of glutaraldehyde and 2.25 g of pTSA dissolved in distilled water were added. The mixture was slowly stirred at 70 °C for 4
h. The resulting polyhydroxy compound glutaraldehyde mixture was symbolized as HBPAEI.

3.8.1.2 Preparation of modified tannin adhesives

Furfuryl alcohol (22 g), water (12.24 g), glyoxal (14.68 g) and HBPAEI (5 g) were added and mixed well in a 250 mL beaker. Subsequently, 22 g of dried tannin extract powder was added gradually to the liquid mixture under constant stirring. pH was adjusted to pH 10 using 33 % (w/v) aqueous NaOH solution. Finally, 6% (w/w) of hexamine was (calculated on the tannin solids basis) dissolved in water to form 30% (w/v) aqueous solution.

3.8.1.3 Blending adhesives of glyoxalated lignin/modification tannin

See section 3.5.3.

3.8.2 Modification of lignin polyol/tannin adhesives by polyethylenimine

Lignin polyols that were prepared from liquefied OPEFB with mixtures of polyethylene glycol (PEG 400) and glycerol (see section 3.6.1) were used for the preparation of water-resistant adhesives, through the mixing with different percentages of polyethylenimine (10, 12, 14, 16, 18, 20%) after dissolving it in very small amounts of water with slight heating at 40 °C. Blending of lignin polyols/tannin adhesive with polyethylenimine ($M_w \sim 25,000$, $M_n \sim 10,000$) took place at room temperature with stirring for 30 minutes.
3.9 Preparation of bio-based wood adhesive from liquefied OPEFB

The procedures of OPEFB liquefaction and synthesis of adhesives are summarized in Figure 3.3. The liquefaction of OPEFB was conducted in a 500 mL round-bottom flask, equipped with a mechanical stirrer, condenser, and thermocouple. The air-dried OPEFB was ground (20-60 wire mesh) using a Wiley mill. Prior to the liquefaction process, the OPEFB was dried in an oven (105 °C, 24 h). Polyethylene glycol (PEG 400) and glycerol were used as liquefaction solvent and sulfuric acid was used as a catalyst.

The ratio between PEG 400 and GLY was 9:1 (w/w). 3% (w/w) of sulfuric acid (based on the solvent content) was used. The mass ratio between dried OPEFB and the used solvent was 1:10 (w/w). Thereafter, 19 g of dried OPEFB was put in the reactor and 187 g of a mixture of PEG 400 and GLY was added together with 5.6 g of 95% (w/v) aqueous sulfuric acid. The contents were mixed in the reactor for about 30 minutes before the liquefaction process for homogeneity. The reactor was immersed in a silicon oil bath that had been heated at 160 °C for 4 h. After the reaction, the reactor was withdrawn from the reaction system and cooled to room temperature in an ice-water bath to quench the reaction. Then, 380 mL of 80% (w/v) 1, 4-dioxane aqueous solution was used to dilute the liquefied product.

The resulting mixture was filtered through a filter paper to remove the insoluble parts of the wood OPEFB. The mixture of 1, 4-dioxane and water was evaporated under reduced pressure after filtration. The pH of liquefied OPEFB was 1.9. Aqueous solution of NaOH (48%) was used to obtain pH 11.5 to 12 of liquefied product. Liquefied OPEFB was placed in a 250 mL flat bottom flask equipped with a condenser, thermometer and magnetic stirring bar and then heated to 70 °C. A quantity of 17.5 parts by mass of glyoxal (40 wt% in water), were added and the
liquefied OPEFB was maintained at pH 11.5-12, with a magnetic stirrer on a hot plate for 8 hours. Finally, 40% glyoxalated liquefied OPEFB was mixed with 60% of tannin adhesives.

![Diagram of liquefaction process](image)

**Figure 3.3:** Synthesis of resol resin from liquefaction of OPEFB

### 3.10 Preparation of organoclay by modification of bentonite

Prior to the bentonite clay modification, purification process to remove impurities from the bentonite clay (BT), which may serve as microfillers, is
necessary so as not to affect the final properties of the resin. The purification process of BT clay was carried out through dispersing the clay in distilled water and left to age for 24 hours to ensure swelling of BT clay. This process enables us to get a solution of colloidal suspension after 12 hours. Thereafter, the BT clay was purified from the supernatant and sediments and then dried in a vacuum oven at 80 °C for 24 hours to remove the moisture. The organically modified BT clay was implemented via an ion exchange reaction between BT and octadecylamine (ODA) salt by dissolving 5 g of ODA in 83 mL of methanol with stirring and the pH adjusted at 5-6 using acetic acid. 10 g of BT clay was added gradually to the above mixture with vigorous stirring for 5 hours and heating at 70 °C. The cation exchange capacity (CEC) ratio of ODA/BT was 1:2.

Finally, the modified BT was collected via centrifugation at 3000 rpm for 15 minutes and subsequently washed several times with deionized water, and then the organic modified bentonite (ODA-BT) was obtained by freeze-drying.

3.11 Modification of lignin polyols/tannin adhesives by bentonite clay

This is the first attempt on liquid phase mixing of the lignin/tannin based wood adhesives with clay. BT or ODA-BT clay was added with different amounts (1, 2, 3, 4, and 5%) to the lignin polyol/tannin resin at room temperature and the whole mixture was stirred overnight (12 hours).

3.12 Preparation of plywood samples

The three-ply veneer with each veneer having a dimension of 150 mm x 150 mm x 2 mm was manufactured using the spread level for a single glue line of
250 g m<sup>-2</sup>. Then it was pressed using a cold press machine with a pressure of 2500 psi, followed by a hot-pressed machine at 140 °C with a pressure of 2500 psi. The total pressing time was maintained at 7 minutes in the cold and hot press. When all the laminated veneer lumber panels were produced, the panels were cut off using a band saw machine to a size of 135 ± 0.2 mm long (in the direction of the face grain) and 25 ± 0.1 mm wide according to the British standard (BS 6566 part 8:1985).

3.13 Characterization of lignins and resins

3.13.1 Preliminary analysis of lignin

The ash content was identified using the proposed method by Mohamad Ibrahim et al. (2011). The lignin powder was obtained by drying the lignin samples at 105 °C in a vacuum oven until constant weight was obtained. Thereafter, approximately 0.5 g lignin samples were weighed and placed in the crucibles and calcined at 900 °C for 4 h. The ash content of the lignin samples was calculated by measuring the weight percentage of lignin samples in the crucible after the burning process. The content of carbon, hydrogen, nitrogen, and sulfur were analyzed using a Thermo Finnigan model Eager 300 analyzer. The percentage of oxygen was measured by subtracting the contents of C, H, N and S from 100%. The percentage of protein was measured as N (%) × 6.25 (Robert et al. 1984; Mohamad Ibrahim et al. 2011). Based on the elemental composition C<sub>a</sub>H<sub>b</sub>O<sub>c</sub>S<sub>d</sub>, the average of double bond equivalent (DBE) was calculated according to Eq. (1) (Robert et al., 1984):
\[
DBE = \frac{(2a + 2) - b}{2}
\]

Eq. (1)

Where

\[a = \text{Molar ratio of carbon}\]

\[b = \text{Molar ratio of hydrogen}\]

pH values of the resins were determined at 30 °C. The viscosity of the resins was determined by a rotary Brookfield viscometer at 30 °C with spindle 3. Solid content of the resins were determined by measuring the weight before and after removing the solvent by heating at 105 °C for 3 hours.

\[
\% \text{ Solid content} = \frac{\text{weight of the solid resin}}{\text{weight of the solution}} \times 100.
\]

3.13.2 Mannich reactivity

The Mannich reactivity examination was carried out to identify the unsubstituted C-3 and C-5 of the aromatic ring in lignin samples as described by Pan & Yoshihiro (1999). Briefly, The mixture of diethylamine (0.6 g) and paraformaldehyde (1.46 g) were dissolved in 90 % dioxane (103 mL). 25 mL of the above solution was added to lignin solution (0.5 g) in 90 % dioxane (25 mL). The mixture was left for one hour at room temperature and was refluxed for another hour. After cooling, the mixture was allowed to evaporate at a temperature below 30 °C under reduced pressure. To remove the free reagents, smaller amounts of mixture of 90% dioxane were added, and the mixture was evaporated again. This process was repeated 3 times. Finally, the residue was dissolved in a small amount of 90%
dioxane and on the precipitate was obtained via freeze-drying. The contents of free C-3 and C-5 were then calculated from the nitrogen content by CHN analysis.

### 3.13.3 Gel time

Gelation is defined as the point at which the resin ceases to be a viscous liquid and becomes a soft, elastic and rubbery solid (Navarrete et al., 2012). A temperature of 100 °C was used for the gel time tests. 5 g of each mixture was put in a glass test tube and then placed in a water bath at 100 °C. A wooden rod was manually moved upward and downward rapidly. A stopwatch was used to calculate the time of gelation.

### 3.13.4 Fourier Transform Infrared (FTIR)

The Fourier Transform Infrared (FTIR) spectroscopy of samples was performed in a direct transmittance mode using a Perkin Elmer model System spotlight 200 instrument. Each spectrum was recorded in a frequency range of 600 cm$^{-1}$ to 4000 cm$^{-1}$ with resolution of 4 cm$^{-1}$ and 20 scans.

### 3.13.5 Acetylation for GPC and NMR analysis

The lignin and lignin polyol samples underwent an acetylation process to improve their solubility in the organic solvent for the gel permeation chromatography (GPC) and NMR analyses. All hydroxyl functional groups were substituted into acetyl groups during the acetylation process. The acetylation was conducted using the method proposed by Thring et al. (1991). Briefly, 30 ml of 1:1 (v/v) mixture of pyridine and acetic anhydride were added to 2 g of lignin in a 100 mL conical flask.
After stirring for 48 h at room temperature, the mixture was treated with 10 volumes of 1\% (v/v) HCl at 0 °C. The resulting precipitate was filtered, washed with deionized water to a neutral pH, and dried at room temperature.

3.13.6 Nuclear Magnetic Resonance Spectroscopy (NMR)

Liquid state $^1$H and $^{13}$C NMR spectra of samples were obtained with a Bruker Avance 500 NMR spectrometer operating at a frequency of 100-59 Mhz. The acetylated lignin, lignopolyol samples and all wood adhesive samples (150 mg) were dissolved in deuterated dimethyl sulfoxide (DMSO-d6) (0.40 mL). Spectral analyses were performed using XW in Bruker software. Quantitative $^{13}$C NMR spectra were acquired at 50 in order to reduce viscosity. Quantitative $^{13}$C NMR spectra were acquired using an inverse-gated decoupling (Waltz-16) pulse sequence to avoid Nuclear Effect (NOE). Forty thousand scans were collected with a pulse delay of 12 s.

3.13.7 Gel Permeation Chromatography (GPC) analysis

Weight average molecular weight ($M_w$), number average molecular weight ($M_n$), and polydispersity index ($M_w/M_n$) were determined by GPC. Tetrahydrofuran (HPLC grade) was used as a mobile phase with a flow rate of 1.0 mL min$^{-1}$ using Water 1525 Binary HPLC Pump. Water Styragel columns, HR 5E THF, and HR 4E THF, as well as a Water 2414 Refractive Index detector, were used. The columns were calibrated using narrow molecular weight monodispersed polystyrene standard ranging from 580 to 8,500,000 g mol$^{-1}$ in the eluent. Briefly, acetylated lignin samples were dissolved in the eluent at a concentration of 10 mg mL$^{-1}$. The solution
was filtered using a 0.45 µm filter. Then, 20 µL of the filtered solution was injected into the HPLC system.

3.13.8 X-ray diffraction analysis

The structural disorder of un-modified bentonite, modified bentonite, and the extent of interaction between silicate layers of bentonite and organo bentonite and resin were investigated by X-ray diffractometer (X’Pert Pro MRD PANalytical - Netherland) with Cu-Kα radiation at a generator voltage of 40 kV and wavelength of 0.154 nm at room temperature. Bragg’s law was used to calculate the basal spacing (d) of the bentonite at wavenumber (λ) and scattering angle (θ). The X-ray diffraction (XRD) patterns of the samples were identified by the X-ray diffractometer within the 2θ =2 -80°.

3.13.9 Scanning electron microscopy (SEM)

The surface morphology of the samples was observed via Leo Supra 50VP scanning electron microscopy (SEM). The samples were sputtered with gold using SC515 Fisons Sputter Coater prior to SEM monitoring. All scanning electron microscopy (SEM) micrographs were taken at an acceleration voltage of 5 kV with a magnification range between 1.00 to 5.00 K.

3.13.10 Thermal analysis

The thermal behaviors of the lignin, lignin polyol, and adhesives samples have been studied by thermogravimetric analysis (TGA) using a Perkin Elmer TGA 7 thermogravimetric analyzer. About 10 mg of sample was put into a platinum
sample pan. Scans were recorded from room temperature to 900 °C with a heating rate of 20 °C min$^{-1}$ under nitrogen atmosphere with a flow rate of 20 mL min$^{-1}$. Curves of weight loss (TG) and derivative weight loss (DTG) were plotted. The glass transition temperatures ($T_g$) were obtained using a Perkin Elmer Pyris 1 differential scanning calorimeter (DSC). The samples were heated up to 200 °C with a heating rate of 20 °C min$^{-1}$.

3.13.11 Mechanical properties

The tensile strength of each sample was measured using an Instron Universal machine (Model 4301), by controlling the rate of the separation of the straining heads which were fixed at 5 mm min$^{-1}$. The distance between the clamps was about 50 mm with the sample being mounted at the center. These tests were performed for the dry, tap water soaked (24 hours) and boiling water soaked (2 hours) bonding sample in order to retain their strength. The water resistance of the plywood composites was evaluated by a water-soaking-and-drying (WSAD) test. The WSAD test was implemented according to the following procedure: the test specimens were soaked in tap water at room temperature for 24 h, and then were dried in a fume hood at room temperature for 24 h and their tensile strength determined.

For the boiling water test (BWT), the specimens were first soaked in boiling water for 2 hours ± 15 minutes, after that the specimens were dried for 20 hours at 60 ± 3 °C. After the drying, the specimens were soaked again in boiling water for 2 hours ± 15 minutes and finally placed in tap water until they cooled down, followed by the tensile strength measurements of the plywood specimens. The plywood
specimens were air dried in a fume hood at room temperature for 24 h and their tensile strength determined. This tensile strength is identified as BWT/dry strength. Wood failure of testing specimens was evaluated by the naked eye from the glueline of destroying specimens. Five samples were tested for each condition.
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Introduction

Attention has been geared towards the production and use of green adhesives for manufacturing wood products. This is due to climate changes and health effects relating to emissions resulting from volatile organic chemicals (VOCs), notably formaldehyde, and the low cost of renewable natural materials compared with petrochemicals.

Production of lignin in large quantities as waste products in the paper industries via various pulping processes have resulted in reviews and intensive studies on the use of lignin in the production of wood adhesives (Muller et al., 2007; Pizzi, 2006).

The aims of this study are to characterize the different types of lignin extracted from oil palm empty fruit bunch (OPEFB) using the different pulping processes and to examine their suitability for the preparation of green phenolic resin through the incorporation of tannin adhesive. Table 4.1 presents the typical chemical composition of OPEFB (Ghazali et al., 2006; Law et al., 2007).

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Ghazali et al., 2006 (%)</th>
<th>Law et al., 2007 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractives</td>
<td>3.7 ± 0.3</td>
<td>3.7 ± 0.3</td>
</tr>
<tr>
<td>Holocellulose</td>
<td>28.4 ± 1.4</td>
<td>28.4 ± 1.4</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>37.0</td>
<td>28.0</td>
</tr>
<tr>
<td>Lignin</td>
<td>18.8 ± 0.3</td>
<td>18.8 ± 0.3</td>
</tr>
<tr>
<td>Ash</td>
<td>1.3 ± 0.2</td>
<td>1.3 ± 0.2</td>
</tr>
</tbody>
</table>

4.2 Investigation of oil palm based lignin as green wood adhesives
4.2.1 Yield of Kraft and organosolv lignin

Table 4.2 shows the elemental composition, ash and moisture content, DBE, and percentage of protein of the Kraft lignin (KL) and organosolv lignin (AEL) extracted from OPEFB derived from the results of the elemental analysis. The proportion of nitrogen was detected for both lignins. The presence of nitrogen content may be attributed to the formation of protein–lignin complexes through the delignification process (Zhao et al., 2009). The remnants of proteins attached to KL were difficult to remove by acid precipitation, revealing that the proteins remained stuck during the pulping process. In particular, this finding suggests that a strong bond exist between the precipitated lignin and the protein in the empty fruit bunch (EFB) fiber, which was difficult to remove even by acid precipitation. Table 4.2 also shows that AEL has lower nitrogen content in the precipitate compared to KL, indicating that the precipitation in AEL is less contaminated.

In addition, the results illustrated that the ash content in AEL (0.02%) is much lesser than that of KL (0.6%), suggesting that the purity of AEL is much higher than that of KL. The ash content ratio in KL is considered as relatively low, and this ratio was reduced after treatment with hot water. It is possible that before treatment with hot water, the KL was attached to sugar, silicon, and wax. The high percentage of sulfur in the KL sample may be derived from the hydrosulfide anions used in the Kraft pulping process of the OPEFB fiber. The number of DBEs in KL equates the degree to which the lignins were condensed and the presence of an aromatic ring structure. The average C9 formulas calculated from the elemental composition were C$_9$H$_{6.4}$O$_{3.93}$S$_{0.27}$N$_{0.06}$ for KL and C$_9$H$_{7.11}$O$_{3.11}$S$_{0.01}$N$_{0.02}$ for AEL. Table 4.2 presents that the number of DBEs of KL was slightly higher than that of AEL. In the Kraft pulping process, it was expected that severe cracking would occur. This cracking is
ascribed to the reaction of hydroxide and hydrosulfide with the lignin. For this reason, the KL structure has higher double bonds compared with that of AEL.

Table 4.2: Ash and moisture contents, elemental composition, protein content, double bond equivalent (DBE) of Kraft and organosolv lignins

<table>
<thead>
<tr>
<th>Type of lignin</th>
<th>Kraft lignin</th>
<th>Organosolv lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash content (%)</td>
<td>0.6</td>
<td>0.02</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>3.79</td>
<td>2.17</td>
</tr>
<tr>
<td>Elemental analysis (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>57.83</td>
<td>65.34</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.42</td>
<td>4.30</td>
</tr>
<tr>
<td>Oxygen</td>
<td>33.66</td>
<td>30.07</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.47</td>
<td>0.19</td>
</tr>
<tr>
<td>Sulfur</td>
<td>4.62</td>
<td>0.10</td>
</tr>
<tr>
<td>Protein (%)</td>
<td>2.94</td>
<td>1.19</td>
</tr>
<tr>
<td>DEB</td>
<td>6.80</td>
<td>6.45</td>
</tr>
</tbody>
</table>

4.2.2 FTIR spectroscopy

The FTIR spectra of KL and AEL are shown in Figure 4.1, and the absorption bands are summarized in Table 1 (Appendix I). A large band at ~3327 cm\(^{-1}\) and ~3404 cm\(^{-1}\) for KL and AEL, respectively, were assigned to phenolic and aliphatic OH stretching vibrations and peaks around 2937 and ~2840 cm\(^{-1}\) were attributed to the symmetrical and asymmetrical C-H. The spectra of KL and AEL showed a difference in the peak intensity of the guaiacyl (G) and syringyl (S) types. Both lignins showed vibration features for the guaiacyl unit bands at around 1269, 1163, 854, and 817 cm\(^{-1}\) attributed to G ring, CH in-plane deformation, and C–H out-of-plane vibrations in position 2, 5, and 6 of guaiacyl units, respectively. The intensity of the bands varied significantly for AEL samples compared with the KL samples. The absorbance at 1324 cm\(^{-1}\) was assigned to a ring breathing of syringyl unit in the AEL samples. However, this band disappeared in the KL samples, indicating the higher syringyl content in AEL. This finding indicates that organosolv
lignin shows quite intense G and S absorption bands. The band vibrations at 849 and 852 cm\(^{-1}\) arose from the C–H out-of-plane in positions 2 and 6 of S units in the KL and AEL, respectively.

![Figure 4.1: FTIR spectra of Kraft and organosolv lignin](image)

Given the different delignification processes, different absorbance intensities are expected in the FTIR spectra. The lower content of S units for KL compared with that of AEL was mainly due to the demethoxylation that took place during the Kraft pulping process (Nadji et al., 2009). Demethoxylation reactions reported during Kraft pulping were indeed exclusive demethylation reactions that occurred under severe reaction conditions that converted more S units to more stable G unit structures within the lignin molecules (Thring et al., 1990). The existence of G-type units in both lignins confirmed that both lignins contain active sites for polymerization.
In the condensation reactions in phenol and formaldehyde, phenol condenses initially with formaldehyde to form methylphenol in the presence of alkali (Pizzi, 1983). The initial attack could be at the 2-, 4-, or 6-position of phenol or 3-position in lignin, as shown in Scheme 4.1. The second stage of the reaction included the reaction of methylol groups with other available phenol or methylolphenol, leading to the formation of linear polymers and then to the formation of curing and highly branched structure. The similarity between G-type units in lignin and phenol (Scheme 4.1) showed that lignin may also react with glyoxal and could be cross-
linked with glyoxal in the same way as in the phenol formaldehyde condensation reaction, as shown in Scheme 4.2. The delignification process used for the separation of lignin plays a substantial role in the final structure (Scheme 4.3). Autocatalyzed ethanol–water pulping process, which uses an ethanol–water mixture as solvent, will liberate the acetic acid from the hemicelluloses that lead to lignin dissolution. This process will boost the acid hydrolysis of lignin and create high-intensity bands of the phenolic hydroxyl (1367 cm$^{-1}$) and carbonyl groups (1708 cm$^{-1}$) in its structure more than Kraft pulping (Faix, 1992; Tejado et al., 2007).

Scheme 4.2: Crosslinking between lignin and glyoxal
Scheme 4.3: Schematic representation of the main changes occurring in the lignin structure during the (a) Kraft, (b) Autocatalyzed ethanol-water processes (Tejado et al., 2007)

4.2.3 $^1$H NMR

The chemical structures of Kraft and organosolv lignins were studied via $^1$H NMR spectrometry. Figure 4.2 shows the $^1$H NMR signals of KL and AEL. As noted in Table 2 (Appendix I), the signal at around 2.5 ppm is indicative of the presence of protons in DMSO. The signals between 6.5 and 7.5 ppm can be ascribed to the aromatic protons in the S and G units. The signals between 0.8 and 1.5 ppm can be attributed to the aliphatic moiety. The methoxy proton exhibited intense signal at around 3.7 ppm, which was closely relevant to the G and S proportion. In addition, aromatic and aliphatic acetyl groups shifted (2.4 ppm to 2.1 ppm and 2.1 ppm to 1.9 ppm, respectively), giving rise to separate peaks (Garcia et al., 2009). AEL showed higher aromatic proton content, where very broad absorption signals of OH were evident. This observation was also consistent with the FTIR results.
Figure 4.2: $^1$H NMR spectra of Kraft and organosolv lignin in DMSO-$d_6$ (500 MHz)

4.2.4 $^{13}$C NMR spectra

$^{13}$C NMR spectroscopy was used to measure qualitatively and quantitatively the different categories of the hydroxyl groups in the lignin and its derivatives. These distinctions between the primary aliphatic, secondary aliphatic, phenolic hydroxyl groups, as well as methoxy groups, are summarized in Table 4.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>KL</th>
<th>AEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic- OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary</td>
<td>0.13</td>
<td>0.38</td>
</tr>
<tr>
<td>Secondary</td>
<td>0.15</td>
<td>0.48</td>
</tr>
<tr>
<td>Phenolic- OH</td>
<td>0.60</td>
<td>0.85</td>
</tr>
<tr>
<td>Methoxy groups</td>
<td>1.11</td>
<td>1.80</td>
</tr>
</tbody>
</table>

The amount of aliphatic and phenolic hydroxyl groups was obtained by the integration of the following regions: primary aliphatic hydroxyl groups (172–169.6 ppm), secondary aliphatic hydroxyl groups (169.6–168.6 ppm), and phenolic hydroxyl groups
(168.6–166 ppm), as shown in Figure 4.3. The amount of methoxy groups was estimated from the integral at 57 ppm. It was observed that the primary and secondary aliphatic hydroxyl groups from AEL are 0.38/Ar and 0.48/Ar, respectively, which are significantly higher compared with those of KL, namely, 0.13/Ar and 0.15/Ar, respectively. The phenolic hydroxyl groups from AEL (0.85/Ar) are slightly higher than those of KL (0.60/Ar). This observation corresponded significantly with previous observations in $^1$H NMR and FTIR.

The integral of the 162 to 102 ppm region was identified as the reference, and was assumed to include six aromatic carbons and 0.12 vinylic carbons. The outcome was used to divide the integral value by 6.12 to obtain the equivalent to the integral value to one aromatic ring (Ar) (Capanema et al., 2004).

![Figure 4.3: $^{13}$C NMR spectra of expanded hydroxyl region of acetylated Kraft lignin and organosolv lignin in DMSO-d$_6$ (125 MHz)](image-url)
The S, G, and \( p \)-hydroxyphenyl (H) units in the spectra were clearly observed with all assignments mentioned in Figure 4.4. Table 3 (Appendix I) presents the signal assignments in the spectra of the acetylated lignin samples (KL and AEL). The signal at around 40 ppm is referred to carbon in DMSO solvent. In agreement with the FTIR results, the AEL exhibited intense signals for the S units that were detected at 104, 139.5, and 152.5 ppm, attributed to the C-2/C6, C-4, and C-3/C5 compared with KL. Meanwhile, the G units in KL produced intense signals at 112, 119, 136.5, and 145 ppm assigned to the C-2, C-6, etherified C-1 and non-etherified C-3 compared with AEL. The strong signals around 172.4 ppm and the moderate signals at 170 ppm are ascribed to the carbon in the carbonyl and carboxyl groups, which may arise from aliphatic esters and aliphatic carboxyls. The strong signals at 168.5, 131, 124.7, and 118.4 ppm (attributed to the C-O-C and C-4, C-2 and C-6, C-1, C-3, and C-5 aromatic carbons, respectively) are signals related to coumaric acid esters (El Hage et al., 2009). The hydroxyphenyl (H) units yielded signals at 127.4 and 128.6 ppm, indicating that both lignin KL and AEL could be referred as GSH grass lignin (Xu et al., 2006).
Figure 4.4: $^{13}$C NMR spectrum of Kraft (KL) and organosolv (AEL) lignins in DMSO-$d_6$ (125 MHz)

The lack of signals between 90 ppm to 102 ppm denotes the low concentration of residual sugar in the two types of lignin (Capanema et al., 2004). The signals at 81.5 ppm (Cβ in S β–O–4 erythro), 72 ppm (Cα in β–O–4 G and S erythro), and 60.3 ppm (Cγ in β–O–4 G and S threo and erythro) are attributed to the β-O-4 linkages.

Figure 4.5: Cα and Cβ linked with -O-4 in S and G structure
The signal at 64 ppm is ascribed to the Cγ with Cα = O; this side chain oxidation may arise from the ball milling extraction method that would decrease the polymerization degree of lignin by homolytic cleavage; the emerging radicals at the side chain would associate with oxygen molecules under aerobic conditions (Xu et al., 2008). The existence of p-coumarate at the γ location of the lignin side chain may also contribute to this signal at 64 ppm (Scheme 4.4) (Crestini and Argyropoulos, 1997). The strong peak at 56.3 ppm is assigned to the methoxy groups in the S and G units. The peaks between 31.7 and 29.4 ppm are assigned to α and β methylene groups, whereas the strong signal at 21 ppm is attributed to CH3 in the acetyl groups. The signals between 15.5 and 14.4 ppm are ascribed to the methylene groups in the n-propyl side chain.

Scheme 4.4: Representation of a coumarylated lignin fragment at the γ position

4.2.5 Molecular weight determination
The weight average (M_\text{w}) and number average (M_\text{n}) molecular weights and polydispersity (M_\text{w}/M_\text{n}) of the KL and AEL samples from GPC analysis are shown in Table 4.4. The results (Appendix II, Fig. 1 and 2) indicate that the weight average (M_\text{w}) of AEL (1231 g mol\(^{-1}\)) is lower than that of KL (1564 g mol\(^{-1}\)) because the AEL undergoes noticeable degradation during the pulping process. These findings can be interpreted according to the different lignin compositions. These results are consistent with other studies mentioned in literature, such as results reported by Hussin et al. (2013) that revealed the molecular weight of Kraft lignin from oil palm fronds was 2063 g mol\(^{-1}\) and organosolv lignin of 1215 g mol\(^{-1}\). In all lignin types, the β-O-4 linkages are most common. However, some important quantities of C-C bonds in the structure units involve C5 of the aromatic ring (Brunow et al., 1999). G-type units have the ability to configure this type of bonds. Notably, this type of bond is not possible in the S types as they have C3 and C5 position substitutions by the methoxy group.

Table 4.4: Weight-average (M_\text{w}) and number-average (M_\text{n}) molecular weights and polydispersity (M_\text{w}/M_\text{n}) of Kraft and organosolv lignins

<table>
<thead>
<tr>
<th>Sample</th>
<th>KL</th>
<th>AEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>M_\text{w} (g mol(^{-1}))</td>
<td>1564</td>
<td>1231</td>
</tr>
<tr>
<td>M_\text{n} (g mol(^{-1}))</td>
<td>597</td>
<td>673</td>
</tr>
<tr>
<td>M_\text{w}/M_\text{n}</td>
<td>2.62</td>
<td>1.83</td>
</tr>
</tbody>
</table>

This feature is important when evaluating the molecular weight of lignins because these C–C bonds are not cleaved during the pulping of wood due to their higher stability. As a result, the lignin that consists strictly of G types is expected to show higher molecular weight than that of S units (Tejado et al., 2007), as also shown in this work. During the Kraft pulping process, repolymerization reactions may occur, affecting the molecular weight of lignins. Some α-hydroxyl groups form quinone methide intermediates under
alkaline conditions may react with other lignin fragments to form alkali-stable methylene linkages (Van der Klashorst, 1989). The severe conditions used in the Kraft pulping encourage such a reaction, which cause the appearance of these high-molecular weight species and lead to high values of the average molecular weight of lignin. Many studies support the use of high-molecular weight lignin fractions in the preparation of phenolic resins (Lange et al., 1983; Olivares et al., 1988a).

Given the larger number of phenylpropane units per fragment, each of these fragments has the ability to contribute to polymerization compared with the monomeric and dimeric fractions (Van der Klashorst, 1989). For this reason, KL would be more appropriate for the preparation of bio-based wood adhesives than the AEL sample. Organosolv pulping process may promote the fragmentation of small-molecular weight lignin (Hage et al., 2010; Pan et al., 2005). The lower polydispersity of AEL (1.83) compared with KL (2.62) indicates high fractions of low-molecular weight components in AEL samples (Alriol et al., 2009). On top of that, the low polydispersity of lignin may lead to higher solubility (Gregorova et al., 2005; Hussin et al., 2013). A study has also reported the advantage of organosolv lignin as a raw material in the production of some low-molecular weight compounds, such as vanillin, hydroxylated aromatics, quinines, aldehyde, and aliphatic acid (Johnson et al., 2005).

4.2.6 Differential scanning calorimetry (DSC)

The glass transition temperature ($T_g$) of amorphous polymers, including lignin, is not easy to be measured precisely due to the influence of several factors, including molecular weight, crosslinking, thermal history, and presence of low-molecular weight contaminants, such as water and solvent (El Mansouri et al., 2011; Hatakeyama, 1992). $T_g$ is considered as the most important thermal property of
polymers, especially in terms of applications and processing (Steven, 1999). Table 4.5 shows that the $T_g$ of KL (154.89 °C) is higher compared with AEL (118.50 °C), which is in accordance with the values reported for different lignin types (between 90 °C and 180 °C) (Lin et al., 2001). $T_g$ of lignin samples (Appendix III, Fig. 1 and 2) can be related to the amount of free volume in the polymer chain and molecular weight. The free volume refers to the space in solid and liquid materials that are unoccupied by polymer molecules (Young and Lovell, 1991).

The high value of $T_g$ (154.89 °C) for the KL sample correlated with the increase in molecular weight and indicates that the main chain of the polymer must have high energy to rotate the chain. The high value of $T_g$ also indicates the presence of few chain ends, resulting in a decline in volume mobility (Jin et al., 2011). Besides, low number average ($M_n$) and high polydispersity values for KL may be associated with such phenomenon. As a result, $T_g$ will be increased. Baumberger et al. (2002) reported that the variations in $T_g$ were closely related to the degree of polymerization of lignin as determined by thioacidolysis by using a series of transgenic poplars. Rigid groups in the main chain and crosslinking restrict molecular motion and increase $T_g$. By contrast, bulky side chains enhance the molecular mobility of lignin through local mode relaxation.

Table 4.5: Values of glass transition temperature ($T_g$), maximum of thermal decomposition temperature (DTG max) and non-volatilized weight fraction at 900 °C (residue) for lignin samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ ( °C )</th>
<th>DTG max ( °C )</th>
<th>Residue ( % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KL</td>
<td>154.89</td>
<td>380</td>
<td>38</td>
</tr>
<tr>
<td>AEL</td>
<td>118.50</td>
<td>360</td>
<td>30</td>
</tr>
</tbody>
</table>

4.2.7 Thermogravimetric analysis (TGA)
Due to a wide variety of applications for lignin, some of which include exposure to high temperatures, considerable research has been conducted on the thermal decomposition of lignin (Lin and Dence, 1990). The TG and DTG of KL and AEL are presented in Figures 4.5A and 4.5B, respectively. The lignin samples degrade in a single step between 105 to 900 °C. Approximately 38% of KL and 30% of AEL non-volatile residues remain intact at 900 °C. These results reveal that KL and AEL are stable at high temperatures, which is attributed to the high degree of branching and formation of highly condensed aromatic structure for both types of lignins.

This behavior is in accordance with the literature data and is attributed to the complex lignin structure that is made up of phenolic hydroxyl, carbonyl groups, and benzylic hydroxyl connected by various types of chemical linkages (Domínguez et al., 2007). These thermal properties have also been observed in phenol formaldehyde resins, marking the similarities between the two types of materials (Tejado et al., 2007).

The initial degradation for lignin samples is ascribed to the loss of water, carbon monoxide, carbon dioxide, and other volatile products from the breaking of the side chains (Hussin et al., 2013; Sun et al., 2001). The second thermal degradation at approximately 280 °C is characterized by the loss of hemicelluloses that are attached to the lignin structure. Similar behaviors have also been observed in some previous studies showing the existence of hemicellulose as a by-product through the precipitation of lignin (Mohamad Ibrahim et al., 2011; Tejado et al., 2007). Hemicellulose was found to degrade at a temperature range of 200 to 300 °C (Garcia et al., 2009; Sun et al., 2000). The maximum thermal decomposition temperature ($T_{\text{max}}$) (Table 4.5) for KL and AEL occurs at approximately 380 °C and 360 °C,
respectively. This temperature region causes the degradation of the complicated structure of lignin samples, including the fragmentation of inter-unit linkages between phenolic hydroxyl, carbonyl groups, and benzylic hydroxyl, which releases monomeric phenols into vapor phase (Alriol et al., 2009).

The thermal stability of the lignin samples increases with increasing molecular weight. The results of TG analysis indicate that KL has a higher thermal stability than AEL. Thus, the introduction of KL in PF formulations or synthesis of green phenolic resin such as glyoxalated lignin-tannin resins, especially those with higher thermal stability, will lead to higher thermal decomposition temperatures. This enhanced thermal behavior may offer wider temperature ranges of applications for lignin in wood adhesives.
4.2.8 Mannich reactivity

The unsubstituted C-3 and C-5 active sites in aromatic rings of lignin are important reactive positions for the synthesis of glyoxalated lignin–tannin. These sites were identified through the Mannich reaction, as shown in Scheme 4.5. The potential use of lignin as wood adhesive is related to the number of active sites on the aromatic rings of the phenolic aryl propane units in the lignin fragments that are capable of reacting with aldehydes like formaldehyde and glyoxal (Pizzi et al., 1989). The free 3- position content in KL (2.99%) is higher than that in AEL (2.06%). This finding indicates that the reactivity of KL with glyoxal is better than that of AEL in glyoxalated lignin–tannin resin, probably due to the higher content of guaiacyl units.
in KL than in AEL, which has a high content of syringyl units (Pizzi et al., 1989). This finding also corresponds with the results of the FTIR.

![Scheme 4.5: Mannich reactivity reaction](image)

**4.3 Preparation of lignin polyols**

In recent times, great efforts have been made to use biomass resource through several methods such as gasification, pyrolysis and liquefaction. Due to its simple preparation, the high level of production, high energy conversion and high capacity of organic materials treatment, liquefaction process has attracted more attention (Ye et al., 2014). Liquefaction process of biomass has progressed in relation to raw materials, solvents, and catalysts. The use of raw materials such as crop residue (Zhang et al., 2012) and wood (Rivas et al., 2013) have been reported. Liquefaction of wood and other lignocellulosic materials with organic solvents, such as phenols and polyhydric alcohols, is a unique thermochemical conversion process in biomass applications because this process combines the useful functional groups of the biomass and organic solvent to obtain a large variety of biopolymers. These biopolymers include coatings (Budija et al., 2009), carbon fibers (Xiaojun and Guangjie, 2010), and adhesives (Fu et al., 2006).
4.3.1 Physico-chemical characteristics of lignin polyols by liquefaction of Kraft lignin and OPEB using polyhydric alcohols

4.3.1.1 FTIR spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to determine the change that occurs in the functional groups of the lignin compounds and their derivatives. The FTIR spectra of the KL and the two polyol samples are shown in Figure 4.6. The assignments of KL spectrum (sample a) are in accordance with previous report (Hussin et al., 2013). A large band at ~3327 cm$^{-1}$ was assigned to phenolic and aliphatic OH stretching vibrations and peaks around 2937 and 2839 cm$^{-1}$ were attributed to CH stretching in the methyl and methylene groups in the side chains and aromatic methoxyl groups. Bands at 1512, 1452, and 1423 cm$^{-1}$ are attributed to aromatic ring vibrations of the phenyl-propane (C9) skeleton. The existence of a band at 1452 cm$^{-1}$, which was caused by C–H deformation (asymmetric) in methyl, methylene, and methoxyl groups, confirms that lignin aromatic structures do not change noticeably during the extraction procedure (Nadji et al., 2009). The absorption bands attributed to syringyl ring with C–O stretching and aromatic C–H in plane deformations are located at 1365 and 1113 cm$^{-1}$. The absorption band at 1030 cm$^{-1}$ is assigned to aromatic CH in the plane deformation for guaiacyl-type lignin.

Comparing to KL (sample a), FTIR spectra of liquefied KL (Sample b) and OPEFB (Sample c) reveal important increase in peaks intensity: at ~1091 cm$^{-1}$ (Sample b) and ~1099 cm$^{-1}$ (Sample c), assigned to aliphatic C-OH groups and ethers (C-O-C) groups (compared with a small peak in Kraft lignin at ~1030 cm$^{-1}$), at 3100-
3700 cm\(^{-1}\) (alcoholic and phenolic OH) and at \(\sim\)2872 cm\(^{-1}\) (aliphatic CH bonds). The significant increase in these peaks intensities can be attributed to the structure of PEG and glycerol.

The liquefied KL (Sample b) and OPEFB (Sample c) reveal that the absorption intensity of methyl groups significantly increased in the new bands at \(\sim\)2872 cm\(^{-1}\). This significant increase in peak intensity can be attributed to two reasons according to Jin et al. (2011). The first reason is that the bonds between the coupling of benzene ring units ruptured, and smaller benzene ring units are formed. The second reason is that the alkylation reaction of the phenolic hydroxyl units of the lignin occurred.

These FTIR results for polyol products are in agreement with reports of other researchers (Jin et al., 2011) for liquefaction of agricultural residues of biomass. The above results could indicate that the liquefaction reaction is caused by a successful chain extension reaction that converts Kraft lignin and lignocellulosic feedstock into polyols.
4.3.1.2 $^1$H NMR spectra

The chemical structures of acetylated Kraft lignin and acetylated polyol products were studied via $^1$H NMR spectroscopy. Figure 4.7 shows the $^1$H NMR spectra of Kraft lignin and lignin polyols. The signal at around 2.5 ppm is indicative of protons in DMSO. Figure 4.7 shows that in KL (Sample a), the signals between 6.5 and 7.5 ppm can be ascribed to aromatic protons in syringyl (S) and guaiacyl (G) units, (6.8 ppm aromatic proton in S unit), (7.4 ppm aromatic proton in G unit) respectively, whereas the signals between 0.8 and 1.5 ppm can be assigned to the aliphatic moiety. In addition, aromatic and aliphatic acetyl groups are shifted differently (2.4-2.1 and 2.1-1.9 ppm respectively). The PEG/ GLY-KL (Sample b) and liquefaction of OPEFB (Sample c) display a significant increase in the peak at
region 3.5 ppm compared with Kraft lignin. This significant increase is probably caused by the presence of polyethylene glycols, glycerol, and ether linkages (C-O-C). The peaks around 3.8 ppm are assigned to the methyl groups, which also show an increase in the intensity compared to the Kraft lignin. This observation is in accordance with the increase of the aliphatic C-H band in FTIR. Strong peaks in the 6.5 ppm to 7.5 ppm regions were assigned to protons from the aromatic rings of KL identified in the lignin polyol samples. These strong peaks in KL spectrum, are however, quite diluted for samples (b) and (c). The peaks observed at 4.5 ppm correspond to proton in hydroxyl groups of the lignin polyols. All these signals seem to confirm that polyols were synthesized through the liquefaction process.

Figure 4.8: $^1$H NMR spectra of (a) KL, (b) liquefied KL with PEG/ GLY, (c) liquefied OPEFB with PEG/ GLY in DMSO-d$_6$ (500 MHz)
4.3.1.3 $^{13}$C NMR spectra

$^{13}$C NMR spectroscopy was used to qualitatively and quantitatively measure the different categories of hydroxyl groups in Kraft lignin and polyol derivatives. The discrimination between the primary, secondary aliphatic and phenolic hydroxyl groups was performed after acetylation and is summarized in Table 4.6. The signal at around 40 ppm is attributed to the carbon in DMSO solvent. The content of aliphatic and phenolic hydroxyl groups were obtained by integration of the following regions: primary aliphatic hydroxyl groups (172.0–169.6), secondary aliphatic hydroxyl groups (169.6–168.6) and phenolic hydroxyl groups (168.6–166.0), as shown in Figure 4.8. The content of secondary aliphatic hydroxyl groups significantly decreased (Jasiukaityte et al., 2010). On the other hand, the content of primary aliphatic hydroxyl groups increased from 0.13/Ar (Sample a) to 0.282/Ar (sample b) and 0.266/Ar (sample c), indicating that lignin polyols were formed by the introduction of soft segments of PEG and glycerol into the lignin structure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount (per Ar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic- OH</td>
<td></td>
</tr>
<tr>
<td>Primary</td>
<td>0.13</td>
</tr>
<tr>
<td>Secondary</td>
<td>0.15</td>
</tr>
<tr>
<td>Phenolic- OH</td>
<td>0.60</td>
</tr>
<tr>
<td>Methoxy groups</td>
<td>1.11</td>
</tr>
<tr>
<td>(a)</td>
<td>0.28</td>
</tr>
<tr>
<td>(b)</td>
<td>0.05</td>
</tr>
<tr>
<td>(c)</td>
<td>0.63</td>
</tr>
<tr>
<td>(c)</td>
<td>0.91</td>
</tr>
<tr>
<td>(c)</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Meanwhile, the NMR spectra of acetylated lignin and lignin polyol samples are given in Figure 4.9. The lack of signals between 90 and 102 ppm indicate that the concentration of sugars that remained in KL is low and can be considered negligible (Capanema et al., 2004). In accordance with the $^1$H NMR results, the peaks between
102 ppm and 162 ppm in Figure 4.9 assigned to aromatic lignin carbons were diluted in the other samples (b and c).

![C-NMR spectra](image)

Figure 4.9: $^{13}$C NMR spectra of expanded hydroxyl region of acetylated (a) KL, (b) liquefied KL with PEG/ GLY, (c) liquefied OPEFB with PEG/ GLY in DMSO-d$_6$ (125 MHz)

The guaiacyl units in the KL (Sample a) produced signals at 112, 119, 136.5, and 145 ppm. The syringyl units were detected by signals at 104, 139.5, and 152.5 ppm in the C-2, C-6, etherified C-1; non-etherified C-3 (for G unit); and C-2/C6, C-4, and C-3/C5 (for S unit), respectively. These peaks, were diluted in the other samples (b and c). This observation concurs with the $^1$H NMR results. The methoxy resonance at around 56 ppm was sharp in KL and decreased, along with a noticeable decrease in aromatic signal in the polyol products (Samples b and c) (Koda et al. 2005). In samples b and c, sharp peaks at 61 ppm, 63.5 ppm, 69 and 73 ppm were assigned glycerol and PEG. A new strong chemical shift was also detected at 70
ppm. This signal could be assigned to benzyl ether type groups formed by the reaction of an alcohol (PEG or glycerol) with the $C_\alpha$ site of the aromatic ring of a phenolic type lignin as shown in Figure (Yong, 2013).

![Proposed structure of lignin attached at $C_\alpha$ aliphatic PEG+GLY](image)

Figure 4.10: Proposed structure of lignin attached at $C_\alpha$ aliphatic PEG+GLY

The $C_\alpha$ linkages should constitute the main intermonomeric linkage because of the process of liquefaction of KL and lignocellulosic feedstock in the presence of a mixture of PEG and glycerol (Yong, 2013).

![13C NMR spectra](image)

Figure 4.11: $^{13}$C NMR spectra of acetylated (a) KL, (b) liquefied KL with PEG/GLY, (c) liquefied OPEFB with PEG/GLY in DMSO-d$_6$ (125 MHz)
4.3.1.4 GPC analysis

The changes in the molecular weight of KL and polyol products were analyzed by using gel permeation chromatography (GPC) (Appendix II, Fig. 3 and 4). GPC was also used to determine the effect of the liquefaction process on Kraft lignin and lignocellulosic feedstock. The weight-average ($M_w$) and number-average ($M_n$) molecular weights and polydispersity ($M_w/M_n$) of the Kraft lignin and lignin polyol samples for GPC analysis are shown in Table 4.7. The increase in $M_w$ and $M_n$ after the liquefaction reaction occurred under acidic conditions. Compared with sample a ($M_w$, 1564 g mol$^{-1}$ and $M_n$, 597 g mol$^{-1}$), a significant increase in $M_w$ and $M_n$ was observed after the liquefaction reaction ($M_w$, 16730 g mol$^{-1}$ and $M_n$, 1200 g mol$^{-1}$ for sample b) and ($M_w$, 12203 g mol$^{-1}$ and $M_n$, 1072 g mol$^{-1}$ for Sample c).

The increase in the molecular weights of the lignin polyols indicates that condensation reactions have occurred between the lignin and multifunctional alcohols. The high molecular weight of samples (b and c) was primarily observed in the condensed structures formed by the incorporation of the aliphatic PEG and glycerol moieties into the lignin structure. The high value of polydispersity indicates that the samples had a wide molecular weight distribution. Most of the research works available in the literature support the utilization of high molecular weight fractions of lignin for the synthesis of modified phenolic resins (Olivares et al., 1988b; Van der Klashorst, 1989).

Table 4.7: Weight-average ($M_w$) and number-average ($M_n$) molecular weights and polydispersities ($M_w/M_n$) of (a) KL, (b) liquefied KL with PEG/ GLY, (c) liquefied OPEFB with PEG/ GLY

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_w$  (g mol$^{-1}$)</td>
<td>1564</td>
<td>16730</td>
<td>12203</td>
</tr>
<tr>
<td>$M_n$  (g mol$^{-1}$)</td>
<td>597</td>
<td>1200</td>
<td>1072</td>
</tr>
<tr>
<td>$M_w/M_n$</td>
<td>2.62</td>
<td>13.94</td>
<td>11.40</td>
</tr>
</tbody>
</table>
4.3.1.5 Differential scanning calorimetry (DSC)

The glass transition temperature \((T_g)\) can be defined as the midpoint of the temperature range at which changes in heat capacity occur. \(T_g\) of an amorphous phase of material is the critical temperature at which the material changes its behavior from glassy to rubbery or vice versa (Young and Lovell, 1991). Samples were dried at 55 °C for 24 h under vacuum to eliminate the moisture before the differential scanning calorimetry technique (DSC) was used. DSC analysis is an established method for measuring polymer \(T_g\). The \(T_g\) of Kraft lignin (154.89 °C), which is in accordance with the values reported for different lignin types (between 90 and 180 °C) (Lin et al., 2001).

Baumberger et al. (2002) showed that the variations in \(T_g\) were closely related to the degree of polymerization of lignin as determined by thioacidolysis by using a series of transgenic poplars. Rigid groups in the main chain and cross-linking restrict molecular motion and increase the \(T_g\). By contrast, bulky side chains enhance the molecular mobility of lignin through local mode relaxation. The \(T_g\) values of polyols resulting from liquefaction of lignin and direct liquefaction of OPEFB (Appendix III, Fig. 3 and 4) show significant decrease, with values of 37.25 and 38.54 °C, respectively, when compared with KL (154.89 °C). This finding shows that the interaction of Kraft lignin and the liquefaction of lignocellulosic feedstock in the presence of a mixture of soft segment of PEG and glycerol, which was copolymerized into a network backbone has resulted in an increase in the free volume and in overcoming the steric effect on the lignin structure, in addition to constituting the blocks side chains. The polymer molecules were which formed from a mixture of PEG and glycerin with lignin chain in the position of \(C_\alpha\), has led to the
increased molecular movement including rotation and vibration, which helped to remarkable decrease in the $T_g$ value.

4.3.1.6 Thermogravimetric analysis (TGA)

The thermogravimetry (TG) technique was extensively used to explain the behavior of the thermal decomposition of lignin and its derivatives. The thermal stability of KL and lignin polyol was studied by TGA. TG curves display the weight loss of substances with respect to the temperature of thermal degradation, whereas the first derivative of the DTG curve exhibits the corresponding rate of weight loss. The peak of this curve ($DTG_{\text{max}}$) is expressed as a single thermal decomposition temperature and can be used to express the thermal stability characteristics of any material. The TG and DTG of KL and lignin polyols are presented in Figure 4.10A and 4.10B, respectively. Thermal degradation of KL includes a wide temperature range between 105 and 900 °C. Approximately 38.1% of non-volatile residue for KL still remains in the solid form at 900 °C and is not completely burned. Approximately 62% of the lignin was lost during the TGA analysis. Studies drawn from the literature review reported that lignin losses 40 to 60% through thermal decomposition (Kubo and Kadla, 2010). KL (Sample a) shows the three thermal cases identified. The first degradation of KL samples from room temperature to approximately 128 °C is characterized by the weight loss of water, carbon monoxide, carbon dioxide, and other volatile products from the breaking of the side chains (Sun et al. 2001; Hussin et al. 2013). The second thermal degradation at approximately 280 °C is characterized by the weight loss of hemicelluloses that are attached to the lignin structure. The hemicellulose was found to degrade at a temperature range of 200 to 300 °C (Garcia et al., 2009; Sun et al., 2000). A similar phenomenon was
observed in earlier reports, thus indicating the existence of hemicellulose as a byproduct of lignin precipitation (Tejado et al., 2007). The maximum thermal decomposition temperature of Kraft lignin (DTG$_{max}$) is approximately 380 °C. This temperature region includes the degradation of the complicated structure of KL, including fragmentation of inter-unit linkages between phenolic hydroxyl, carbonyl groups, and benzylic hydroxyl, which releases monomeric phenols into vapor phase (Alriol et al., 2009).

Lignin polyol (Samples b and c) exhibited slightly greater thermal stability than KL. Samples b and c also showed significantly similar features of the weight loss and maximum decomposition temperature. DTG curves of polyols presented with peaks ranging from 147 °C to 311 °C and 311 °C to 410 °C (Sample b), from 168 °C to 316 °C and 316 °C to 410 °C (Sample c). These results are in accordance with those of Briones et al. (2012) on the DTG analysis of pure PEG-glycerol, which presented a glycerol decomposition from 153 °C to 267 °C and PEG decomposition from 267 °C to 392 °C. The results of weight losses in the lignin polyol samples were relatively high, at 89.8% for sample b and 86.9% for sample c. The higher weight loss of the polyol products may be attributed to the presence of the moieties of PEG and glycerol. This thermal behavior supports the hypothesis of the use of lignin polyols in the applications of phenolic resins within a wide temperature range.
Figure 4.12: (A) TG curves and (B) DTG curves of (a) KL, (b) liquefied KL with PEG-GLY, (c) liquefied OPEFB with PEG/GLY
4.3.2 Physico-chemical characteristics of lignin polyols by liquefaction of Kraft lignin using propylene oxide

4.3.2.1 FTIR spectroscopy

The FTIR spectra of the starting material and the Kraft lignin-based polyol products (KL + PO) are shown in Figure 4.11. The modified oxypropylated lignin displays new bands at 2873 cm\(^{-1}\) attributed to methyl groups of the grafted propylene oxide units and increased significantly with the absorption peak intensity of methylene groups at 2928 cm\(^{-1}\), an absorption band at 1377 cm\(^{-1}\) corresponding to CH, and bands at 1026 and 1124 cm\(^{-1}\) caused by the presence of primary and secondary OH groups. Lignopolyol exhibits greater increase in peak intensity of OH groups than the corresponding OH groups in KL, indicating that the oxypropylation process between Kraft lignin and propylene oxide had indeed occurred. The FTIR results suggest that oxypropylation reaction succeeded in converting Kraft lignin into polyols.

The oxypropylated sample indicates an increase in the intensity of absorption region at 3100–3500 cm\(^{-1}\) that is attributed to the presence of propylene oxide oligomers in the oxypropylation mixture. Finally, the broad band 3300–3500 cm\(^{-1}\) in the liquefied sample indicates the presence of OH groups in the liquefied product.
Compared with the starting Kraft lignin, the oxypropylated lignin exhibits obvious differences in the $^1$H NMR spectral data (Figure 4.12). The signal at around 2.5 ppm is indicative of protons in DMSO. Introducing large amounts of PPO grafts created peaks of 1.1, 3.5, and 3.8 ppm attributed to CH$_3$-O, CH$_2$-O, and CH-O groups, respectively. Most of the propylene oxide was reacted either to form the lignin polyol or the homopolymer of polypropylene oxide (PPO), which are two competitive reactions during oxypropylation process. This phenomenon is evident through $^1$H NMR, which confirms that in the case of the methyl signal of the monomer (PO), the doublet is not noticeable because of the broadening influence of the molecular size of the oligomer and the polymer structure of the PO homopolymer chains. In the NMR spectra of polymers, peaks enlarge and lose their multiplicity.
with increasing macromolecular size (Nadji et al., 2005). In addition, strong peaks in the 6.5 ppm to 7.5 ppm region are assigned to protons from aromatic rings of Kraft lignin identified in the lignin polyol samples, although these peaks are quite diluted because of the dominance of PPO grafts (Faris et al., 2015). These signals confirm that polyol production was undertaken through oxypropylation process (Scheme 4.6).

![Figure 4.14: ¹H NMR spectra of Kraft lignin and oxypropylated lignin in DMSO-d₆ (500 MHz)](image)

Scheme 4.6: Schematic diagrams of direct oxypropylation methods of hydroxyl groups in lignin
4.3.2.3 Molecular weight determination

The effects of oxypropylation reaction on Kraft lignin structure were evaluated using changes in molecular weight. Weight-average ($M_w$) and number-average ($M_n$) molecular weights and polydispersity ($M_w/M_n$) of the Kraft lignin and lignopolyol samples for GPC analysis (Appendix II, Fig. 5) are shown in Table 4.8. The increase in $M_w$ and $M_n$ after oxypropylation reaction occurred under alkaline conditions. The obtained lignin polyol products showed increased molar masses, indicating that condensation reactions between Kraft lignin and multifunctional alcohols have occurred. In addition, the high value of polydispersity indicates that the samples had a wide molecular weight distribution. The results are compatible with the results of FTIR and NMR analysis.

Table 4.8: Results of weight-average ($M_w$), number-average ($M_n$) and polydispersity ($M_w/M_n$) of Kraft lignin and polyol products

<table>
<thead>
<tr>
<th>Sample</th>
<th>KL</th>
<th>KL+PO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_w$  (g mol$^{-1}$)</td>
<td>1564</td>
<td>2566</td>
</tr>
<tr>
<td>$M_n$  (g mol$^{-1}$)</td>
<td>597</td>
<td>729</td>
</tr>
<tr>
<td>$M_w/M_n$</td>
<td>2.62</td>
<td>3.52</td>
</tr>
</tbody>
</table>

4.3.2.4 Differential scanning calorimetry (DSC)

The $T_g$ of Kraft lignin (153.42 °C), which is in good agreement with the values reported for different lignin types (between 90 and 180 °C). The $T_g$ for lignin modification (Appendix III, Fig. 5) has decreased significantly to 41.98 °C. This reduction is essentially ascribed to the increase in free volume of lignin polyol molecules as the hydroxyl groups increase. The concentration of chain ends is attributed to the introduction of OH groups, which contributes to an increase in free volume of the polyol products. The glass transition could be described by such
activation energies using free volume. The chains in lignin initially vibrate when energy is supplied. By adding more energy, the lignin chains rotate and create free volume. This behavior has also been observed in lignin esters (Glasser and Jain, 1993).

4.3.2.5 Thermogravimetric analysis (TGA)

The thermal stability of Kraft lignin and lignin polyol was studied by TGA. The TG and DTG of Kraft lignin and polyol products are obtainable in Figures 4.13A and 4.13B. Comparison with Kraft lignin, the thermal decomposition temperature (DTG_{max}) decreases considerably with oxypropylation reaction; that is, the hydrophilic character of the sample decreases correspondingly. The thermal stability curves represent two events of degradation. The introduction of propylene oxide (PO) causes a decrease in the degradation temperature of the oxypropylated product from 287 to 180 °C and from 380 to 340 °C due to the higher thermal crispness of the polyethers (Menezes et al., 2007).
Figure 4.15: (A) TG curves and (B) DTG curves of Kraft lignin and oxypropylated lignin
4.4 Preparation of water resistant wood adhesives

Glyoxalated lignin-tannin adhesives are good candidates for the replacement of formaldehyde based adhesives because of health and environmental concerns. Although glyoxalated lignin-tannin resins are low cost and have environment friendly properties, these types of adhesives do not meet the fundamental required bonding strength and water resistance (Charles, 2005; Pizzi and Mittal, 2003). In addition, poor water resistant property has limited their application. Ease of hydrolysis makes this adhesive useful for interior applications only. Consequently, appropriate measure must be taken to overcome the problem and to improve the water resistance of adhesives. In this work, we tried to develop and improve the properties of glyoxalated lignin-tannin resin to meet the fundamental requirement of bonding strength and water resistance.

4.4.1 Preparation and characterization of green adhesives using modified tannin and hyperbranched poly (amine-ester).

Due to the unique structure, chemical and physical characteristics and various industrial applications, hyperbranched polymers (HBPs) have become the focus of considerable interest to chemists, biochemists, biologists, and biomedical experts (Bharathi and Moore, 1997; Fréchet et al., 1995; Magnusson et al., 2000). This is due to high solubility, reduction of melt and solution viscosity and abundance of functionalities as a result of the large number of reactive terminal groups within a molecule, nearly spherical molecular shape and the absence of chain entanglement (Fang et al., 2008; Gao and Yan, 2003; Jikei and Kakimoto, 2001). These characteristics make dendrimers and hyperbranched polymers (HBPs) applicable as
drug-delivery agents, catalysis, Mitchell mimics, nanoscale building blocks to artificial cells and coatings (Gao et al., 2003; Khan et al., 2006; Salazar et al., 2001). Both dendrimers and hyperbranched polymers are three dimensional and highly branched macromolecules (Malmstrom and Hult, 2001, 1997). In this work, oligomeric precursors of poly (amine-ester) were synthesized, and then they were used to modify the tannin to improve the water resistance and mechanical properties of glyoxalated lignin-tannin (GLT) based wood adhesives. Scheme 4.7 shows the synthesis of hyperbranched poly (amine-ester).

Scheme 4.7: Synthesis of hyperbranched poly (amine-ester)
Previous studies by Lei (2009) indicated the use of GL/PF/pMDI formulation with calcium lignosulfonate and it turned out that the molecular mass decreased significantly during thermal treatment at 170 °C for 90 min and pH of 12.7. This has been done to reduce the molecular mass of the lignin. Some linkages of lignin are broken by thermal treatment and positions that are more reactive will be obtained. This indicates that the thermal treatment will make the material more suitable for such reactions. In this work, two types of low molecular mass lignins extracted from oil palm empty fruit bunch were used. These are (i) Kraft lignin (ii) Organosolv lignin. The adhesive resins properties are shown in Table 4.9.

Table 4.9: Variation of the physical properties of CPF, TGKL and MTGKL resins

<table>
<thead>
<tr>
<th>Resin type</th>
<th>Viscosity at 30 °C, 100 rpm (cP)</th>
<th>Solid Content a (%)</th>
<th>pH</th>
<th>Gel Time at 100 °C (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPF</td>
<td>190</td>
<td>59.80</td>
<td>11.30</td>
<td>480</td>
</tr>
<tr>
<td>TGKL</td>
<td>65</td>
<td>39.26</td>
<td>9.46</td>
<td>164</td>
</tr>
<tr>
<td>MTGKL</td>
<td>108</td>
<td>53.08</td>
<td>9.30</td>
<td>235</td>
</tr>
</tbody>
</table>

aSolid content of the resins was determined by measuring the weight before and after removing the solvent by heating at 105 °C to constant weight. %Solid content = (weight of the solid resin/weight of the solution) x 100.

4.4.1.1 FTIR spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to investigate the preparation of HBPAE and the change that occurred in the functional groups. The FTIR spectra of the \(N,N\)-diethylol-3-amine methylpropanoate (AB2) and hyperbranched poly (amine-ester) (HBPAE) are shown in Figure 4.14. The broad band at \(~3387\ \text{cm}^{-1}\) was assigned to stretch vibrations of hydroxyl groups in AB2. The obvious absorption peaks at 1437 and \(1361\ \text{cm}^{-1}\) are assigned to bending vibration absorption peaks of OH. HBPAE shows increasing absorption intensity at ~
3335 cm\(^{-1}\) due to the appearance of many terminal hydroxyl groups on the periphery of hyperbranched poly (amine-ester). The bands at 2951 and 2878 cm\(^{-1}\) in AB2 and the bands at 2934 and 2879 cm\(^{-1}\) in HBPAE are due to symmetric and asymmetric C-H. Comparing with AB2, the absorption of ester carbonyl at 1732 cm\(^{-1}\) in HBPAE is significantly decreased, whereas the absorption intensity of C-N at 1612 cm\(^{-1}\) in HBPAE is significantly increased, which indicates the reaction of hyperbranched poly (amine-ester). The peaks at 1180 and 1028 cm\(^{-1}\) in AB2 and peaks at 1187 and 1032 cm\(^{-1}\) in HBPAE are assigned to C–O–C and C–N, respectively. The absorption of C=C at 1619 cm\(^{-1}\) in AB2 has a weak intensity, indicating that most of the double bonds in methyl acrylate have been consumed by the reaction of Michael addition.

Figure 4.16: FTIR spectra of (a) N,N-diethylol-3-amine methylpropanoate (AB2) (b) hyperbranched poly (amine-ester) (HBPAE)

Tannin glyoxalated Kraft lignin resin (TGKL) and modified tannin glyoxalated Kraft lignin resin (MTGKL) were analyzed using FT-IR to compare
against commercial phenol-formaldehyde (CPF) resin. Figure 4.15 depicts the FTIR spectra of all resins. The broad absorption OH peaks for TGKL, MTGKL and CPF appeared at 3350, 3348 and 3336 cm$^{-1}$, respectively. In TGKL and MTGKL, these broad peaks are caused by the presence of hydrogen bonds from alcoholic and phenolic hydroxyl groups in lignin (Grushnikov and Elkin, 1973; Sarkanen, 1987). The absorption band at 1634 cm$^{-1}$ and the large peak at 1547 cm$^{-1}$ are attributed to the C-H vibration in the aromatic ring of the phenyl-propane (C9) skeleton of the TGKL. MTGKL shows a peak at 1630 cm$^{-1}$ and a small peak at 1505 cm$^{-1}$, whereas CPF displays the C-H vibration of the aromatic ring at 1639 cm$^{-1}$.

In TGKL and MTGKL spectra, the broad peaks absorption at 1348 cm$^{-1}$ and 1349 cm$^{-1}$ regions are observed which are attributed to Kraft lignin, assigned to the C-O of syringyl unit (Khan et al. 2004a). However, this peak has disappeared in CPF. The most important peaks at 1237 cm$^{-1}$ and 1222 cm$^{-1}$ in TGKL and MTGKL, sequentially are assigned to C-C and C-O-C. These peaks indicate the introduction of the glyoxal into the lignin molecule, thus confirming the glyoxalation reaction between Kraft lignin and glyoxal (El Mansouri et al., 2011). Meanwhile, the bands at 1086 and 1076 cm$^{-1}$ in TGKL and MTGKL are characteristics of lignin and are attributed to the C-O of primary alcohol (Saad et al., 1980). The stretching of aliphatic ethers linkage C-O-C, are indicated by the absorption peaks at 1011 cm$^{-1}$, 1006 cm$^{-1}$ and 1014 cm$^{-1}$ of TGKL, MTGKL and CPF, respectively. The band at 1006 cm$^{-1}$ in MTGKL shows a significant increase in intensity due to C-N linkages.
The chemical structure of \(N,N\)-diethylole-3-amine methylpropionate (AB2)
and HBPAE were studied via \(^1\)H NMR spectrometry. Figure 4.16 shows the \(^1\)H NMR
spectra of AB2 and HBPAE. The signal at 2.5 ppm is indicative of the presence of
protons in DMSO. In \(^1\)H NMR of AB2, the signal at 2.43 ppm indicates the protons
in \(\text{CH}_2\) which is attributed to ester units. The signal at 3.20 ppm can be assigned to
\((\text{NCH}_2\text{CH}_2\text{OH})\). The peaks around 3.34 ppm can be ascribed to the peak of –
\(\text{OCOCH}_2\text{CH}_2\text{NR}_2\). The multiple signals at 3.5 ppm could be due to \(\text{CH}_2\) in the units
\((\text{HOCH}_2\text{)}\). The peak at 3.67 ppm can be attributed to methyl groups in the ester units
\((\text{COOCH}_3\text{)}\). The absorption peak of vinyl hydrogen is not found, indicating that the
Michael addition of diethanolamine and methyl acrylate was completed successfully.
All these signals belong to AB2 monomer. \(^1\)H NMR spectrum of HBPAE shows
distinct signals of chemical shifts at 0.7 ppm which is attributed to \((\text{CH}_2-\text{(CH}_3\text{)}\text{CH} –
NCH₂⁻), whereas the signals of the chemical shift at 1.2 ppm is assigned to (CH₃CH₂⁻) and other signals at 2.0-2.3 ppm are ascribed to (-N(CH₂CH₂OH)₂). The chemical shift at 3.20 ppm of (-NCH₂CH₂OH) has disappeared, indicating that a polymeric reaction has happened. The absorption signal at 4.7 ppm is attributed to (-CH₂CH₂OH).

Figure 4.18: ¹H NMR spectra of (a) N,N-diethylol-3-amine methylpropanoate (AB2) (b) hyperbranched poly (amine-ester) (HBPAE) in DMSO-d₆ (500 MHz)

The ¹H NMR of the three liquid adhesive resins shows important differences in the spectra (Fig. 4.17). The chemical shift at 6.5-7 ppm corresponds to the aromatic proton rings in the TGKL, showing the existence of more free positions in the aromatic rings of resins. These signals are reduced in the MTGKL due to steric hindrances. An absence of chemical shift in the range 7.0-7.5 ppm for CPF spectrum shows that the aromatic rings are less substituted (Pérez et al. 2007). The TGKL and MTGKL resins exhibit a higher level of substitution at the aromatic ring. The peaks
in the 4.2-4.4 ppm range correspond to methyl groups and the 4.6 ppm zone can be attributed to methylene linkages with phenyl groups (Ar-CH₂-Ar). Strong signals at 6.3 and 6.4 ppm are ascribed to methylol groups (CH₂OH) and (-NCH₂CH₂OH), respectively, whereas the strong signal at 7.5 ppm is attributed to (-NCH₂COOCH₂) groups, belonging to MTGKL.

Figure 4.19: ¹H NMR spectra of resins for (a) TGKL (b) MTGKL (c) CPF in DMSO-d₆ (500 MHz)
4.4.1.3 $^{13}$C NMR spectra

It was observed that, $^1$H NMR spectra did not illustrate sufficiently on the complexity of the chemical structure of the liquid adhesive resins, most probably due to the overlapping of signals. Thus, the $^{13}$C NMR technique was used to further obtain information by identifying a greater number of functional groups. Due to the very complex structure of lignin, the (TGKL) and (MTGKL) have a large number of signals due to the presence of lignin functional groups.

$^{13}$C-NMR chemical shifts of TGKL, MTGKL and CPF are obvious in Figure 4.18. The peak at 40 ppm is attributed to the presence of carbon in DMSO solvent. The absence of the peaks at 170-180 ppm suggests that the aliphatic carboxylic acids were not formed during the preparation of the three liquid resins, which might make the interaction of curing resin more difficult (Pérez et al., 2007). The chemical shifts at 168 ppm, correspond to carbonyl group in MTGKL (Luukko et al., 2001; Werstler, 1982). This feature can be also observed in the $^1$H NMR spectra (Fig. 4.17), which can explain the presence of ester groups and linkages with the aromatic rings of the tannin due to the modification reaction with hyperbranched poly (amine-ester). This signal is not present in TGKL. Due to variations of its environment, the chemical shifts of phenolic carbon are located between 150 and 168 ppm (Woodbrey et al., 1965). The spectrum of CPF shows the peaks from 164 to 168 ppm which are attributed to carbons that are attached to the phenolic hydroxyl groups. The typical signal of 123.7-129.5 ppm of commercial phenol formaldehyde resin is due to C3 and C5 carbons of the phenolic ring substituted in its ortho position by methylene bridges (Holopainen et al., 1997).

The aromatic carbon that is linked to OH group arises at 154.7 ppm of MTGKL and in region between 150 to 165 ppm for TGKL. The absence of
resonance intensity in the range of 80-90 ppm indicates the consumption of glyoxal during the reaction between glyoxal and Kraft lignin and the lack of any forms of unreacted aldehyde in TGKL and MTGKL resins (George et al., 1991). The chemical shift zone of 61-62.9 ppm and 63-64 ppm, is directly attributed to the ortho and para hydroxymethyl carbons position of the phenolic ring in CPF (Nieh and Sellers, 1991). $^{13}$C resonance intensity in the range of 61-72.5 ppm region can be attributed to the $\alpha$, $\beta$ and $\gamma$ carbons in the lignin structure. These peaks also indicate that the methylene ether bridges were formed during the synthesis of TGKL resin (Pérez et al. 2007). MTGKL resin shows weaker resonance intensity at 62.5 ppm compared with TGKL resin probably due to the dominance of modification of tannin and steric hindrance. The methoxy group from the Kraft lignin components is clearly observed at 55.4 ppm in the spectrum of the MTGKL resin.

Figure 4.20: $^{13}$C NMR spectra of resins for (a) TGKL (b) MTGKL (c) CPF in DMSO-d$_6$ (125 MHz)
4.4.1.4 Thermal stability

Figure 4.19 (A and B) shows the TGA and DTG curves of the TGKL, MTGKL and CPF resins. Decomposition temperatures and percentages of non-volatile residue (char content) are tabulated in Table 4.10. It is obvious that the initial weight loss (T\textsubscript{onset}) of CPF, TGKL and MGK at 80, 110 and 125 °C, correspond to the weight loss of 7, 17 and 6 % respectively, due to the loss of moisture and captured water. It is mentioned that there is a similarity in the thermal features of the phenol formaldehyde resin with lignin (Tejado et al., 2007). The maximum degradation temperatures (T\textsubscript{max}) occur in three stages. During the first stage, when the temperature rises from room temperature to 200 °C, the weight loss of the resins is mainly caused through dehydration, aldehyde as well as the degradation of other volatile products from the breaking of the side chains (Sun et al. 2001; Hussin et al. 2013). Water elimination could lead to the formation of new cross-links (Chen et al., 2008; Costa et al., 1997).

For temperatures above 300 °C the resins undergo further degradation. The weight loss is due to the release of water, which is produced from the condensation reaction between the methylene groups and phenolic OH groups and between two hydroxyl functional groups. In this step, water is considered as the main contributors to the weight loss. During the third stage, when the temperature reaches 600 °C, major polymer degradation takes place (Chen et al., 2008; Costa et al., 1997) and crosslinking between ethylene and carbon-hydrogen leads to hydrogen elimination. In addition, it leads to the formation of products such as carbon monoxide and methane due to the reaction of the water and hydrogen that are produced with the methylene group. Furthermore, random chain cleavage and the initial formation of char could also take place (Costa et al., 1997; Shulman and Lochte, 1996).
Comparing TGKL and MTGKL, the modification of tannin may affect the resin structure and become more heat-resistant than TGKL as a result of the incorporation of the poly (amine-ester) in the tannin structure which is decomposed at temperatures about 200 °C. Therefore, it increases the crosslinking reaction in the resin. This is evident from the high temperature degradation and increase in the content of non-volatile materials compared with TGKL (Erä and Mattila, 1976; Manley, 1989).

### Table 4.10: TGA data on CPF, TGKL and MTGKL resins

<table>
<thead>
<tr>
<th>Resin type</th>
<th>$T_{\text{max}1}$ (°C)</th>
<th>$T_{\text{max}2}$ (°C)</th>
<th>$T_{\text{max}3}$ (°C)</th>
<th>Residue at 900 °C, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPF</td>
<td>80</td>
<td>151</td>
<td>380</td>
<td>63.1</td>
</tr>
<tr>
<td>TGKL</td>
<td>110</td>
<td>120</td>
<td>220</td>
<td>48.9</td>
</tr>
<tr>
<td>MTGKL</td>
<td>125</td>
<td>170</td>
<td>310</td>
<td>72.6</td>
</tr>
</tbody>
</table>
Figure 4.21: (A) TG curves and (B) DTG curves of resins for TGKL, MTGKL and CPF
4.4.1.5 Tensile Strength of Phenolic Resins

The quality of wood and how the resin penetrates through the wood surface are important factors that affect the assessment of the adhesive joint in plywood. The bonding strength formed by TGKL and MTGK adhesives were studied via tensile strength (Appendix IV) test on wood substrates. For a comparative study, the same test was implemented for synthetic commercial phenol formaldehyde resin. The data is displayed in Table 4.11.

The maximum load, tensile strength, elastic modulus and elongation at break of panels are direct measures of the performances. From Table 4.11, the trend shows that the dry MTGKL resin has the highest maximum load of 5506.9 N with a tensile strength of 39.72 MPa and elongation at break of 21.91%. This result indicates that MTGKL resin is stronger than that of the CPF resin. TGKL has the highest maximum load of 3720.57 N with a tensile strength of 28.79 MPa and elongation at break of 20.61%. That is also stronger than that of the CPF resin but lesser than MTGKL resin. The results of MTGKL and TGKL resins are within the requirement of the relevant international standard as per British Standard for dry tensile strength of plywood (≥0.35 MPa) (British Standard, 1985).
Table 4.11: Tensile strength, elastic modulus and elongation at break of plywood using CPF, TGKL and MTGKL resins

<table>
<thead>
<tr>
<th>Resin type</th>
<th>Tensile Strength MPa</th>
<th>Elastic modulus MPa</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DRY</td>
<td>Cold water soaking 24 h</td>
<td>Boiling water soaking 2h</td>
</tr>
<tr>
<td>CPF</td>
<td>1.39</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>1.25</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>---</td>
<td>1.01</td>
</tr>
<tr>
<td>TGKL</td>
<td>28.79</td>
<td>Delamination</td>
<td>---</td>
</tr>
<tr>
<td>MTGKL</td>
<td>39.72</td>
<td>---</td>
<td>Delamination</td>
</tr>
<tr>
<td></td>
<td>---</td>
<td>27.62</td>
<td>---</td>
</tr>
</tbody>
</table>

Interestingly when comparing TGKL with MTGKL resins, the water resistance of MTGKL resin is improved after modification with poly (amine-ester). This is evident in the results of tensile strength (27.62 MPa) after soaking the plywood samples of MTGKL resin in tap water for 24 hours at room temperature, where no delamination occurred in any of the specimens. However, delamination was observed in the plywood samples of TGKL resin after soaking in water for a period not exceeding one hour, indicating the lack of water resistance for TGKL resin when it was used to bond plywood. This suggests that the modification of tannin by adding oligomeric precursors (hydroxyl-terminated) of a hyperbranched poly (amine-ester) is successful to boost the network structure of natural phenolic resin to prepare a water resistant resin.

The improvement of water resistance of MTGKL resin is assumed to be due to the reaction of the terminal units of glutaraldehyde with the hydroxyl groups of tannin and with –NH₂, -COOH. Other exposed groups lead to an increase in the cross-linking density within the resin in the hot pressing process and consequently,
there will be an increase in the mechanical properties. In addition, the presence of furfuryl alcohol as a cross-linking agent and its participation in increasing the cross-linking reaction, help to improve the water resistance of MTGKL based wood adhesives. The whole process is represented in Scheme 4.8.

Scheme 4.8: Proposed mechanism for the participation of formulation components in crosslinking reactions and improvement of water resistance properties for the resulting modified tannin-glyoxalated lignin (Li et al., 2012)
4.4.2 A combination of lignin polyols-tannin adhesives and polyethylenimine for preparation of green water resistant adhesives

Protein adhesive, which was secreted via marine mussels, called marine adhesive protein (MAP), is a good example of a renewable resource and formaldehyde adhesive (Waite, 1990, 1987). MAP has the ability to form strong linkages on wet surfaces and thus could be used as a strong and water-resistant wood adhesive (Waite, 1990, 1987). However, they are costly and not readily available. MAP contains two functional groups (catechol and amino groups). The different reactions between the catechol group and the amino group lead to the crosslink and solidification of the MAP, thereby converting the MAP to a very strong and very water-resistant adhesive (Rzepecki and Waite, 1991; Waite, 1990).

Condensed tannins and lignin are one of the few natural polymers containing a catechol moiety (Glasser 1981; Li, et al. 2004). Previous studies showed the possibility of using a combination of condensed tannins or lignin and polyethylenimine (PEI) to synthesize wood adhesives. Figure 4.20 shows representative structures of polyethylenimine. This adhesive has high shear strength and exhibits significant water resistance (Geng and Li, 2006; Li et al., 2004; Liu and Li, 2006). In this work, wood adhesive system, which consists of a tannin glyoxalated lignin polyols (TGLP) and PEI were evaluated for plywood, and compared to plywood produced with a glyoxalated lignin/tannin and conventional phenol formaldehyde resin.
4.4.2.1 Effect of the solid content of TGLP-PEI adhesives on tensile strength

It was observed that, an increase in the total solid content of the TGLP-PEI adhesives leads to an increase in its viscosity. Moreover, when the total solid contents in adhesives reached 55%, the TGLP-PEI adhesives became too viscous. It can clearly be seen from Figure 4.21 that the total solid contents increased from 48.54 to 56.92% when the ratio of PEI was changed from 10 to 20% in TGLP resin. The tensile strengths (dry, WSAD, and BWT/dry) of wood composites bonded with the adhesives have revealed a dramatic increase in its values (63.04, 59.48, and 53.53 MPa), respectively, and a linear relationship among all values. The TGLP-PEI adhesives with total solids contents (56.92%) were applied to plywood and used in subsequent experiments.

The production of wood composites does not favor the use of wood adhesives with low solid contents due to higher energy consumption and comparatively longer time of water evaporation through hot press. In the current study, a significant amount of the total solid contents of adhesives (56.92%) was obtained during the modification of lignin polyols-tannin resins with polyethylenimine. There was a substantial difference in the solid contents of modified (56.92%), unmodified
adhesives (45.82%) and the commercial phenol formaldehyde (59.50%) under the same experimental conditions. The solids content of the TGLP resin (45.82%) was lower than the solids contents of the CPF resin (59.50%). However, the solids contents of the TGLP-PEI resins were almost comparable to the CPF resin, especially when the ratio of PEI was 20% in TGLP-PEI resin. It is known that CPF resins contains large amount of urea and for this reason, the solid content value is very high (Zhao, 2013).

Figure 4.23: Effect of total solids content of TGLP–PEI adhesives on tensile strength (dry, tap water soaking for 24 h, and boiling water soaking for 2 h) comparison with TGLP and CPF
4.4.2.2 Effect of the solid content of TGLP-PEI resin on the gel time

The total solid contents of TGLP-PEI adhesives have a strong influence on the gelation time. As shown in Figure 4.22, the gelation time of TGLP-PEI adhesives decreased with increasing solid contents of adhesives. With the increase in total solid contents in the system, a corresponding decrease in the water quantity present in the adhesive system was observed. This has led to an increase of the crosslinking reaction whereby these water molecules did not serve as energy barrier during the curing process. Thus, the cure rate gets increased leading to a shorter gel time. It is therefore essential to control the moisture contents of the material during the manufacturing of the wood-composite products.

Figure 4.24: Effect of the solid content ratio of the gel time of the TGLP-PEI resin
4.4.2.3 Effects of PEI weight ratios on tensile strengths and water-resistances of wood composites bonded with TGLP–PEI adhesives

Some earlier researches have proven that the TGLP adhesives are more effective in bonding to plywood (Mansouri et al., 2010; Taylor et al., 2012). However, the current findings revealed that the combination of TGLP and PEI possess even stronger bonding capability towards plywood (Appendix IV). The weight ratio of the PEI had a significant impact on the tensile strength and water resistance of the wood composites bonded with TGLP-PEI adhesives (Fig. 4.23). The TGLP adhesive has a dry tensile strength of 31.1 MPa, but delaminated during a WSAD treatment and BWT/dry treatment. At 10% weight ratio of PEI in TGLP, the dry tensile strength of the resulting plywood samples was relatively higher (35.57 MPa) than the TGLP. At this percentage of PEI, the delamination of resulting plywood samples did not occur when it underwent the WSAD and BWT/dry treatment, and the plywood samples retained with a high strength. All three tensile strengths (dry, WSAD, and BWT/dry) significantly increased when the weight ratio of the PEI in TGLP increased from 10 to 20% as compared to the TGLP and CPF resins. It can be inferred that, modification of TGLP with PEI significantly increases the tensile strength and water resistance of the resulting plywood samples. On possible explanation would be, this increase is due to further reactions between the amino groups of PEI with catechol moieties present in both lignin and tannin it could increase the amount of cross-linking in the resin and ultimately increases the tensile strength and water resistance.
Some possible reactions between lignin and tannin with PEI

To date, the reactions between lignin and tannin as well as PEI, are not fully understood. Some of the proposed potential reactions are given in Scheme 4.9. The nature of TGLP-PEI resins curing mechanisms is comparable to the quinone-tanning methods as reported elsewhere (Waite, 1995). Moreover, the reaction mechanisms between lignin and PEI are mostly similar to the possible reactions between tannin and PEI (Li et al., 2004b). At elevated temperatures, the catechol moiety (2) in the demethylated lignin is highly vulnerable to oxidation process leading to the formation of quinones (3). This occurs at higher temperatures (140 °C) using a hot press during the formation of wood composites. The quinones (3) possibly reacts with the amino groups present in PEI structure, thus forming Schiff bases (4 and 5). Some other possible reactions between quinones and amino groups of PEI (such as Michael addition reaction) may also occur to form (6) and further Schiff bases (7 and
8). A similar kind of reaction occurs during the oxidation process to form phenolic hydroxide in lignin structure during hot press, which further results in the formation of quinone. It further supports the increase of the reactions with amino groups of PEI to form Schiff bases.

It is well known that wood has lignin, which contains phenolic hydroxyl groups, and these groups can be oxidized to quinone during the hot press, hence they cannot be excluded from the covalent bond formation between TGLP-PEI adhesive and wood. In addition to the reaction of the quinone, the catechol moiety can react with the amino groups of PEI and form strong hydrogen bonds. Furthermore, it can also form strong hydrogen bonds with the hydroxyl groups in the wood components (see a representative structure 9 and 10 in Scheme 4.9). It can be inferred from these reactions that, the curing reactions through the hot press process leads to the formation of highly cross-linked TGLP-PEI network polymers, as well as water resistant adhesives. These results, are in close agreement to mechanical tests and proven through soaking plywood samples bonded with TGLP-PEI adhesives in the tap water and boiling water.
4.4.2.5 Thermal stability

Thermal stability of thermoset polymers, heavily depends on the structure of the polymer and the crosslinking density (Erä and Mattila, 1976; Manley, 1989). It is an important feature describing the durability of polymer. The thermal degradation (TG and DTG) curves of TGLP and TGLP-PEI are presented in Figures 4.24A and 4.24B, respectively. It was found that the thermal features of phenol formaldehyde

Scheme 4.9: Some possible reactions between tannin and PEI
resin with lignin is similar to the reported literature (Tejado et al., 2007). The maximum degradation temperatures ($T_{\text{max}}$) of TGLP and TGLP-PEI resins was quite similar to the thermal degradation of commercial phenol formaldehyde resin, which follows an auto-oxidization process, and mainly involve three stages.

During the first stage, when the temperature rises from room temperature to 200 °C, the weight loss of the resins is mainly due to the loss of water through dehydration, loss of aldehyde as well as the degradation of other volatile products coming from the breaking of the side chains (Hussin et al., 2013). Water elimination can lead to the formation of new cross-links (Chen et al., 2008). For temperatures above 300 °C, the resins undergo further degradation. The weight loss is due to the release of water, which is produced from the condensation reaction between the methylene groups and phenolic OH groups.

In the third stage, when the temperature reaches 600 °C, major polymer degradation takes place (Chen et al., 2008) and crosslinking between ethylene and carbon-hydrogen leads to hydrogen elimination. In addition, it leads to the formation of products such as carbon monoxide and methane due to the reaction of the water and hydrogen, which were produced with the methylene group. Furthermore, a random chain cleavage and the initial formation of char could also take place (Shulman & Lochte, 1996).

The thermal behavior of the TGLP and TGLP-PEI resins differs significantly. The modification of TGLP via incorporation of the PEI can affect the TGLP resin structure by increasing the crosslinking density of resin and therefore become more heat-resistant. From Figure 4.24B, two distinct thermal degradation (DTG) peaks in the temperatures range of 200 to 370 °C for the TGLP-PEI resin were observed and the results are shown in Table 4.12.
In the TGLP resin, the maximum degradation temperatures ($T_{\text{max}}$) is 125 °C and at this temperature, the major polymer decomposition occurred. Whereas, the major polymer decomposition in TGLP-PEI occurred at the 360 °C. These findings are in close agreement with the mechanical properties of TGLP-PEI, especially in the boiling water.

Table 4.12: TGA data on the TGLP and TGLP-PEI resins

<table>
<thead>
<tr>
<th>Resin type</th>
<th>$T_{\text{max}1}$ (°C)</th>
<th>$T_{\text{max}2}$ (°C)</th>
<th>$T_{\text{max}3}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPF</td>
<td>80</td>
<td>151</td>
<td>380</td>
</tr>
<tr>
<td>TGLP</td>
<td>80</td>
<td>125</td>
<td>225</td>
</tr>
<tr>
<td>TGLP-PEI</td>
<td>70</td>
<td>190</td>
<td>360</td>
</tr>
</tbody>
</table>
Figure 4.26: (A) TG curves and (B) DTG curves of resins for TGLP, TGLP-PEI and CPF
4.5 Synthesis and characterization of resol type tannin glyoxalated liquefied wood (TGLW) resin

The liquefaction of wood and other lignocellulosic materials with organic solvents, such as phenols and polyhydric alcohols, are a unique thermochemical conversion process in biomass applications because this process combines the useful, functional groups of the biomass and organic solvent to obtain a large variety of biopolymers (Pan, 2011) and has been studied extensively by many researchers.

Most of the studies and research were conducted to investigate the use of phenol as liquefaction solvent and formaldehyde as a curing agent (Ahmadzadeh et al., 2008; Atta-obeng, 2011). However, no attention has been given to use the glyoxal as a curing agent with liquefaction of OPEFB using polyhydric alcohols. However, the aim of the current study is to make an attempt to use glyoxal as a curing agent in the synthesis of wood adhesives from liquefaction of OPEFB and combined with tannin adhesive. The adhesive properties are shown in Table 4.13.

Table 4.13: Variation of the physical properties of CPF and TGLW resins

<table>
<thead>
<tr>
<th>Resin type</th>
<th>Viscosity at 30 °C,100 rpm (cP)</th>
<th>Solid Content(^a) (%)</th>
<th>pH</th>
<th>Gel Time at 100 °C (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPF</td>
<td>190</td>
<td>59.5</td>
<td>11.3</td>
<td>480</td>
</tr>
<tr>
<td>TGLW</td>
<td>81</td>
<td>43.8</td>
<td>9.5</td>
<td>204</td>
</tr>
</tbody>
</table>

\(^a\)Solid content of the resins was determined by measuring the weight before and after removing the solvent by heating at 105 °C to constant weight. %Solid content = (weight of the solid resin/weight of the solution) x 100
4.5.1 FTIR spectroscopy

FTIR spectra of the TGLW and CPF resins are shown in Figure 4.25. OPEFB biomass is mainly composed of lignin, hemicelluloses and cellulose. In general, the resol-type TGLW resin exhibited a similar FTIR absorbance to the CPF resin. The broad absorption peak at 3337 cm\(^{-1}\) in TGLW is attributable to the OH stretching vibrations due to the presence of alcohol and phenolic hydroxyl groups in lignin, hemicelluloses and cellulose as well as the moisture contents in the specimens inevitably (Baki et al., 2012; Sarkanen, 1987) and the moisture contents in the fibers. The absorption bands at 1632 and 1542 cm\(^{-1}\) can be assigned to the C=C vibration in the aromatic ring of phenyl-propane (C9) skeleton of TGLW, indicating the presence of phenolic compound in liquefied OPEFB, whereas in CPF this C=C vibration of the aromatic ring was found at 1639 cm\(^{-1}\). The absorption band in CPF resin at 1446 cm\(^{-1}\) represent the C = C in the benzene ring, which obscured the -CH\(_2\)- methylene bridge that appear generally at 1478 cm\(^{-1}\) (Atta-obeng, 2011).

In TGLW resin, absorption band at 1452 cm\(^{-1}\) is ascribed to the O-H in-plane deformation and to the C=C bonds in the aromatic rings as well as an asymmetrical stretching of CH\(_3\) and CH\(_2\). The large peak intensity at 1347 cm\(^{-1}\) in TGLW resin was due to the C-O of syringyl unit in lignin (Khan et al. 2004a). However, this peak has disappeared in CPF. The most important peak at 1251 cm\(^{-1}\) in TGLW resin is assigned to the C-C, C-O-C and C=O groups. These peaks indicate the introduction of the glyoxal onto liquefied OPEFB structure, thus confirming the glyoxalation reaction between liquefied OPEFB and glyoxal (El Mansouri et al., 2011). Meanwhile, the band at 1083 cm\(^{-1}\) in TGLW resin is a characteristic band of lignin and is attributed to the C-O of primary alcohol (Saad et al., 1980). The absorption peaks at 1041 cm\(^{-1}\) indicate the stretching of aliphatic ethers linkage C-O-C, and
1014 cm\(^{-1}\) of TGLW and CPF resins, respectively. The C-O-C linkage in TGLW belongs to the cellulose and hemicellulose structures (Zhao, 2013).

![FTIR spectra of TGLW and CPF resins](image)

Figure 4.27: FTIR spectra of TGLW and CPF resins

4.5.2 \(^1\)H NMR spectra

The \(^1\)H NMR of the TGLW and CPF liquid adhesive resins indicated some important differences in the spectra (Fig. 4.26). The signal at around 2.5 ppm attributed to the protons in DMSO. The chemical shift in the TGLW at 6.5-7.0 ppm can be ascribed to the aromatic proton rings in the syringyl (S) and guaiacyl (G) units in lignin. This showed the existence of more free positions in the aromatic rings of resin, indicating that the liquefied OPEFB is very effective towards glyoxal. An absence of chemical shifts in the range of 7.0-7.5 ppm for CPF spectrum showed that
The aromatic rings were less substituted (Pérez et al., 2007). The TGLW resins show a higher level of substitution in the aromatic ring.

The chemical shift at 8.4 ppm belongs to syringyl C5 phenolic hydroxyl and phenolic hydroxyl in TGLW and CPF, respectively. The signals in the range of 4.2-4.4 ppm range are attributable to methyl groups whereas the 4.6 ppm zone can be assigned to the methylene linkages with phenyl groups (Ar-CH2-Ar). The TGLW resin shows a significant increase in the chemical shift in the 3.4 ppm region. This substantial increase may be due to the presence of glycerol and polyethylene glycol as a medium for liquefaction of OPEFB as well as the existence of ether linkages (C-O-C).

Figure 4.28: \(^1\)H NMR spectra of TGLW and CPF resins in DMSO-d\(_6\) (500 MHz)
4.5.3 \textsuperscript{13}C NMR spectra

\textsuperscript{13}C-NMR chemical shifts of TGLW and CPF are obvious in Figure 4.27. The peak at 40 ppm is attributed to the presence of carbon in DMSO solvent. The presence of chemical shift at around 177 ppm can be attributed to the C=O group of the aliphatic carboxylic acids (glucuronic acid), which was formed during the preparation of the TGLW resin. This observation suggested the esterification to lignin, which can make the interaction of curing resin easier (Pérez et al., 2007; Zhao, 2013). The absence of the peaks at 170-180 ppm indicates that the aliphatic carboxylic acids were not formed during the synthesis of the CPF resin. The signal at 172 ppm could be attributed to the primary aliphatic OH groups, whereas the peak at 168 is assignable to the secondary aliphatic OH and carbonyl groups in TGLW, respectively. (Luukko et al., 2001). The carbonyl groups in the TGLW resin may have arose from the liquefied OPEFB, or through the oxidation process of the phenolic rings or both simultaneously.

The spectrum of CPF showing the peaks from 164 to 168 ppm, are attributable to the carbons that are attached to the phenolic hydroxyl groups. The typical signal between 123.7-129.5 ppm of CPF resin is due to C3 and C5 carbons of the phenolic ring substituted in its ortho position by methylene bridges (Holopainen et al., 1997). Moreover, the OH group that is linked to aromatic carbon appeared at 159 ppm and for TGLW resin. The chemical shift at high intensity (135 ppm) can be attributed to C1 in guaiacyl (G) and syringyl (S) units in lignin. The chemical shifts between 102 ppm and 162 ppm were attributed to the aromatic rings in the resin. Figure 4.27 shows the high intensity signals in these ranges, indicating that the phenolic contents in TGLW resin was high because of the liquefied OPEFB components of cellulose, hemicellulose and lignin with high phenolic contents. This
leads to the high reactivity of liquefied wood, showing better crosslinking reactions with glyoxal and this would reflect upon the improved resin properties. Furthermore, it supports their use in humid weather and hence the preparation of water resistant wood adhesives.

The absence of chemical shifts in the range of 80-90 ppm suggested the consumption of glyoxal during the reaction between glyoxal and liquefied OPEFB and the lack of any form of unreacted aldehyde in TGLW resin (George et al., 1991). The chemical shift zones of 61-62.9 ppm and 63-64 ppm, are directly attributed to the ortho and para hydroxymethyl carbons position of the phenolic ring in CPF (Nieh and Sellers, 1991). The large intensity of chemical shift in the range of 60-72 ppm in TGLW can be assigned to the α, β and γ carbons in the lignin molecule. These signals confirmed that the methylene ether bridges were formed during the preparation of TGLW resin (Pérez et al., 2007). These signals can give an indication that the liquefied OPEFB are highly reactive and can easily react with glyoxal to form methylol groups. However, the intensities of the chemical shifts of methylol groups and methylene groups in the TGLW resin were stronger than those of the CPF resin, suggesting that the liquefied OPEFB had high reactivity.
4.5.4 Tensile Strength of Resins

The bonding strength formed by resol-type TGLW and CPF resin as adhesives was evaluated through tensile strength (Appendix IV) tests of plywood samples (under both dry and wet conditions). The maximum load, tensile strength, elastic modulus and elongation at break of panels are illustrated in Table 4.14. Tensile strength tests clearly demonstrated that the tensile strength for both dry and wet plywood specimens by a TGLW was stronger (21.4, 19.71 MPa) than the CPF (1.39, 1.25 MPa), respectively. As can be seen from Table 4.14, the trend displays that the dry TGLW resin has a tensile strength of 21.4 MPa with a higher maximum load of 3208.3 N and elongation at break of 16.3%.
Interestingly, the results of dry TGLW resin surpassed the minimum requirement of the relevant international standard as per British Standard for dry tensile strength of plywood (≥0.35 MPa) (British Standard, 1985) and also JIS K-6852 standard (i.e., 1.2 MPa) for resole-type adhesives. In addition, when soaked TGLW resin specimens in tap water for 24 h at room temperature, no delamination occurred in any of the specimens. This behavior is probably due to the high reactivity of resol-type TGLW resin as adhesives and leads to an increase in the cross-linking density within the resin in the hot press cure and consequently, there would be an increase in the wet tensile strength. This finding was also consistent with the $^1$H NMR and $^{13}$C NMR results. Surprisingly, however, the tensile strength values were still comparable and exceeded the minimum value of wet tensile strength (1.0 MPa) required by JIS standard.

Table 4.14: Tensile strength, elastic modulus and elongation@ break of plywood using CPF and TGLW resins

<table>
<thead>
<tr>
<th>Resin type</th>
<th>Max. Load (N)</th>
<th>Tensile Strength MPa</th>
<th>Elastic modulus MPa</th>
<th>Elongation @ break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DRY</td>
<td>Cold water 24 h soaking</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPF</td>
<td>183.02</td>
<td>1.39</td>
<td>56.61</td>
<td>12.45</td>
</tr>
<tr>
<td></td>
<td>164.78</td>
<td>1.25</td>
<td>41.10</td>
<td>15.84</td>
</tr>
<tr>
<td>TGLW</td>
<td>3208.3</td>
<td>21.40</td>
<td>171.3</td>
<td>16.30</td>
</tr>
<tr>
<td></td>
<td>2493.2</td>
<td>19.71</td>
<td>186.6</td>
<td>15.04</td>
</tr>
</tbody>
</table>

4.5.5 Thermal stability

The thermal stability of the TGLW resol and CPF resins were investigated by TGA technique. Figure 4.28A and 4.28B include the TG and derivative of TG (DTG) results of the resins between 30 °C and 900 °C in an N$_2$ atmosphere. The maximum
degradation temperatures ($T_{\text{max}}$), percentages of non-volatile residue, and char content at 900 °C are listed in Table 4.15.

<table>
<thead>
<tr>
<th>Resin type</th>
<th>$T_{\text{max}1}$ (°C)</th>
<th>$T_{\text{max}2}$ (°C)</th>
<th>$T_{\text{max}3}$ (°C)</th>
<th>Residue at 900 °C, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPF</td>
<td>80</td>
<td>151</td>
<td>380</td>
<td>63.10</td>
</tr>
<tr>
<td>TGLW</td>
<td>125</td>
<td>225</td>
<td>360</td>
<td>69.70</td>
</tr>
</tbody>
</table>

As described in Figure 4.28B, the DTG curves for the TGLW resol and CPF resins exhibited three similar degradation events, reflecting the three steps decomposition of phenolic resin: post-curing, thermal reforming and ring stripping (Khan and Ashraf, 2007; Vázquez et al., 2002). For the CPF resin, the first maximum degradation event that starts from room temperature to 200 °C, may be due to the post curing reaction in the resin including the removal of water, aldehyde, and degradation of other volatile products from the breaking of the side chains and further condensation reaction, as well as the transformation of the ether bridges to methylene bridges (H. M. Hussin et al., 2013; M. A. Khan et al., 2004; Sun et al., 2001).

The second maximum thermal event above 300 °C may be attributed to the thermal reforming, involving breaking of the methylene bridges and the interaction between the methylene groups and phenolic OH groups. During the third event, when the temperature reaches 600 °C, major polymer decomposition occurred because of the breakdown of the ring network (Chen et al., 2008). The TGLW resol resin underwent several decomposition patterns and showed similar DTG profiles of CPF resin with three thermal degradation steps at room temperature to 259, 259 to 438 and 438 to 600 °C, with maximum degradation temperatures ($T_{\text{max}}$), as given in Table 4.15.
Figure 4.30: (A) TG curves and (B) DTG curves of resins for TGLW and CPF.
Due to a high thermal stability of TGLW, high efficiency shown by the liquefied wood during the reaction with glyoxal and their ability to form a lot of crosslinking reactions, the heat resistance properties in the TGLW resol resin have improved.

### 4.6 Influence of Bentonite Clay on Lignin Polyols as Wood Adhesives

Improving the polymer properties through incorporation a second component such as additives to obtain new materials have become common. Inorganic additives are frequently used in the wood adhesives industry that improve the mechanical and thermal properties of resins (Pizzi et al., 1994). Recently, utilization of the montmorillonite to modified phenolic resin attract significant interest of researchers to improve some properties such as stiffness and toughness (Choi and Chung, 2003; Jiang et al., 2006; Jonathan et al., 2005; Lee and Giannelis, 1997; Wang et al., 2002). In this work, wood adhesives system, consisting of a tannin glyoxalated lignin polyols (TGLP) was modified using bentonite and organo bentonite clay and then evaluated on plywood.

#### 4.6.1 FTIR spectroscopy

The FTIR analysis spectra of unmodified BT and ODA-BT provide evidence on the organic modification process of bentonite. The FTIR patterns for both BT and ODA-BT differed significantly (Fig.4.29). The absorption peak of OH bending at 916 cm\(^{-1}\) is attributed to the Al–OH that was readily assigned. The strong absorption band centered at 1007.5 cm\(^{-1}\) is ascribed to Si–O stretching vibration. The peaks at 3392.6 and 1627 cm\(^{-1}\) allocated from bending and stretching vibrations of hydroxyl
groups from molecules of water, respectively (Fenandes et al., 2007; Zagorka and Aleksandra, 2007).

The peak at 3623 cm\(^{-1}\) represents the Al(Mg-OH). These spectra belong to the basic skeleton of BT. The spectra of ODA-BT give all the above absorption peaks that appeared in the spectrum of BT, however, there are new absorption bands in Figure 4.29 that are due to the intercalated organo-modifier. The absorption peaks at 2917 and 2849 cm\(^{-1}\) are attributed to the asymmetric and symmetric stretching vibrations of C-H groups in octadecylamine structure, respectively, which indicates that the modification of bentonite by ODA occurred, and also indicating the existence of long alkyl chain in the bentonite (García-Lopeza et al., 2005; Shichang et al., 2008). Also, a new absorption peak at 1516.6 cm\(^{-1}\), ascribed to the bending vibrations of methylene groups further support this finding (Sankaraiah et al., 2007).

In the FTIR spectrum of ODA-BT, it was observed that the absorption bands at 3392.6 and 1627 cm\(^{-1}\) that were attributed to the OH groups in water molecules disappeared, suggesting that the basal cations are exchanged completely and the hydrophilic nature of bentonite was reduced due to the introduction of ODA groups. Similar observation was mentioned by previous studies (Co’tica et al., 2011; Huskić et al., 2009; Zhang et al., 2010).
Figure 4.31: FTIR Spectra of unmodified BT and modified ODA-BT

4.6.2 X-ray diffraction

X-ray diffraction (XRD) analysis technique is most widely used for the characterization of clay or organoclay structures and gives the basal spacing values. It can also identify the shape, position, and intensity of the basal reflection from the silicate layers as well as intercalation, where extended polymer chains occupy the interlayer space between silicate layers or exfoliated, where the silicate layers are dispersed in a continuous polymer matrix may be identified. The XRD analysis illustrates a characteristic peak because of regular layered structures.

Unmodified-BT, ODA-BT, TGLP adhesive with both BT and ODA-BT structures were investigated via XRD analysis as shown in Figure 4.30 that refers to the 2θ values from 2–80°. The 2θ and d spacing values (d_{001}) are listed in Table 4.16. From the XRD pattern, it is clear that the BT has a diffraction peak appearing at 5.60, which corresponds to basal spacing of 15.84 nm. In the ODA-BT sample, the
diffraction peak was shifted to lower angle ($2\theta = 4.80$) with basal spacing of 18.50 nm. These results demonstrated that the layer silicates galleries of the BT were expanded because of the modification of surfactants and intercalation of a long-chain of alkyl ammonium cations group in the silicate layer of BT.

Table 4.16: $2\theta$ and d spacing (nm) data of unmodified BT, ODA-BT, and composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta$</th>
<th>d spacing, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT</td>
<td>5.60</td>
<td>15.84</td>
</tr>
<tr>
<td>ODA-BT</td>
<td>4.80</td>
<td>18.50</td>
</tr>
<tr>
<td>TGLP-BT</td>
<td>14.30</td>
<td>6.29</td>
</tr>
<tr>
<td>TGLP-ODA-BT</td>
<td>4.65</td>
<td>18.98</td>
</tr>
</tbody>
</table>

As expected, due to the non-crystalline state (amorphous) of lignin, which forms a high percentage of the TGLP adhesive, the resin with bentonite clays does not appear on the XRD pattern. According to previous studies, many polymers expand when incorporated with clays (Aranda and Ruiz-Hitzky, 1992; Shen et al., 2002; Triantafillidis et al., 2002). It was found that the basal spacing of the TGLP-ODA-BT shifted to lower diffraction angles ($2\theta = 4.70$) when compared with TGLP-unmodified-BT ($2\theta = 14.30$) as shown in Figure 4.30. The basal spacing increased significantly for TGLP-ODA-BT (18.98 nm) compared with TGLP-BT (6.2 nm), suggesting the successful insertion of TGLP resin into organo bentonite galleries. As expected, the chemical nature of the organo bentonite modifier has a remarkable influence on the extent of bentonite intercalation.
Figure 4.32 XRD patterns of un-modified BT, modified BT, and composites

4.6.3 SEM with EDX analysis

SEM is a significant technique used to interpret changes in morphology of bentonite during a modification process by surfactants. SEM micrographs of bentonite before and after modification with ODA as well as the SEM images of composites with adhesive are shown in Figure 4.31. The corresponding elemental analysis data are summarized in Table 4.17. It is worth mentioning that there are no substantial differences in morphology between natural and organic bentonite, despite the obvious differences, which were observed in the FTIR and XRD spectra as well as TG analysis (discussed in 4.6.5).

The unmodified BT (Fig. 4.31a) demonstrated huge aggregated morphology with large sized particles in the structure. Some fragments of small sized particles in
BT structure were relatively regular. This may be due to the interactions of face-to-face and face-to-edge of particles (Garci’a-Lopeza et al., 2005). Comparing with the unmodified BT, the BT-ODA (Fig. 4.31b) showed smaller particles and irregular shapes as well as more severely aggregated particles than BT. In addition, the SEM images also revealed the expansion that took place in layers of silica and a more open structure in the ODA-BT. As a result, further exfoliation during composites fabrication is expected.

SEM analysis of BT-TGLP composites in Figure 4.31c exhibited the lack of compatibility between the unmodified bentonite and matrix resin, which could lead to the formation of tactoids. During the modification of organic bentonite using appropriate modifiers, the interaction between the matrix resin and the organo bentonite would be sufficient for a certain degree of exfoliation and/or intercalation even when forming the tactoid. SEM micrograph of ODA-BT containing the composite resin is given in Figure 4.31d. As shown in Figure 4.31d, ODA-BT particles were dispersed in the TGLP matrix and the resulting composite structure (TGLP-ODA-BT) demonstrated a highly homogenous distribution.
Elemental analysis by EDX of the BT, ODA-BT, and composites (Appendix V) are shown in Table 4.17. Energy spectra indicate that elements present are C, Si, Al, and O. From Table 4.17 the BT sample has the highest content of silicon (Si) and aluminum (Al). It is clear that the bentonite is a class of aluminum silicate minerals. For ODA-BT, it was observed that the amount of carbon (C) element (21.12 w%) has significantly increased compared with BT sample (12.79 w%) indicating the presence of alkyl ammonium cations as intercalant group in the bentonite gallery that additionally supports the modification that occurred. It is noteworthy to point out that the percentage of all the other elements such as Si and Al, decreased significantly and this can be due to the presence of carbon (C).
Table 4.17 EDX Elemental analysis of unmodified BT, ODA-BT, and composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (w%)</th>
<th>O (w%)</th>
<th>Si (w%)</th>
<th>Al (w%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BT</td>
<td>12.79</td>
<td>61.05</td>
<td>17.96</td>
<td>5.73</td>
</tr>
<tr>
<td>ODA-BT</td>
<td>21.12</td>
<td>68.84</td>
<td>6.22</td>
<td>1.97</td>
</tr>
<tr>
<td>TGLP-BT</td>
<td>22.42</td>
<td>67.14</td>
<td>3.95</td>
<td>1.21</td>
</tr>
<tr>
<td>TGLP-ODA-BT</td>
<td>23.22</td>
<td>66.39</td>
<td>0.72</td>
<td>0.64</td>
</tr>
</tbody>
</table>

4.6.4 Tensile Strength of TGLP-bentonite composites

The average tensile strength of unfilled TGLP resin and composite with corresponding bentonite and organo-bentonite loadings were determined from tests conducted on at least five plywood specimens under dry conditions as shown in Figure 4.32. The tensile strength of TGLP composite (Appendix IV) has been considerably improved by incorporating both BT and ODA-BT.

The tensile strength of TGLP composite increases non-linearly with BT and ODA-BT content. From Figure 4.32, the dry tensile strength was more effected by ODA-BT than BT. The reason in the strengthening of tensile properties is probably due to intercalation/exfoliation of the bentonite structure in the phenolic matrix of adhesives. As the silicate layer in bentonite structure has excellent mechanical characteristics compared with TGLP, the enhanced mechanical properties of resin may be linked to the dispersion level of the silicate layers into the matrix of resin. It is believed that the dispersion process of clay in polymer chain provides a large interfacial interaction that may cause a restriction on the mobility.
There are multiple factors that affect the mechanical properties including the ratio of filler, dispersion of the filler, and the adhesion at the filler matrix interface (Isik et al., 2004; Wang et al., 2004). In addition, the exfoliation degree of the silicate layer in the polymer affect the modulus of composites (Kornmann et al., 2001; Zerda and Lesser, 2001). This reveals that the significant increase of the tensile strength modulus through the incorporation of low contents of ODA-BT (1, 2, and 3 wt%) can be due to uniform dispersion of nanoparticles at such a low content. High content of particles (4 and 5 wt%), reduced the dispersion and thus restricts the improvement of tensile strength (Fig. 4.32). The Elastic modulus has the same sensitivity toward dispersion. Dispersion of filler particles has less effect when BT is used, the limitations of tensile strengths shows at a loading of 5% (Fig. 4.32).
The decrease of the tensile strength at high content of BT and ODA-BT can be attributed to the agglomeration of particles. An agglomeration of particles could also serve as crack initiation sites, as well as the non-uniform distribution. Through the results, it could be concluded that the use of ODA-BT is better than BT to improve the mechanical properties, particularly tensile strength when used in low concentrations. This can possibly be due to lower silicate layers in the ODA-BT compared to BT because of the organic modification of bentonite, that has a positive effect on ODA-BT, thus increased the crosslinking density.

With the modification of bentonite, the ODA-BT became more compatible with the TGLP resin chains, due to the decrease of surface energy of bentonite layers, thus the surface polarity of ODA-BT is compatible with the resin polarity. The ODA-BT with lowered surface energy has more ability to interact and intercalate within the interlayer space of resin than BT, thus improves the various properties of the resin.

4.6.5 Thermal stability

In order to study the role played by fillers on the thermal degradation of composites, thermal gravimetric analysis (TGA) was conducted in N₂ atmosphere with heating rate of 20 °C min⁻¹. Figure 4.33A, 4.33B, 4.34A and 4.34B show the TG and DTG curves of unmodified BT, ODA-BT, and composites, respectively. For natural bentonite, two main degradation stages can be observed. The first degradation that occurred below 120 °C gives the maximum temperature degradation of 78 °C with a weight loss of 13%. During this stage the weight loss could be attributed to the removal of surface adsorbed water (Huskić´ et al., 2009). The peak at 480 °C that was accompanied by a weight loss of 15% could be ascribed to the elimination of
interlayer water. These water species necessitate temperatures much higher than those associated with the surface (Michail et al., 2005; Thontree et al., 2008).

In the second degradation stage between 500-800 °C, the TG curves gave a weight loss around 17.4 %. The weight loss at this stage is ascribed to the dehydroxylation in the structure of clay layers. The release of hydroxyl structure at 640 °C is in agreement with the classical range of dehydroxylation temperature (600–7008 °C) (Co’tica et al., 2011). Beyond 675 °C the bentonite clay loses its structure and practically shows no weight loss (Araujo et al., 2004).

The TG and DTG curves of ODA-BT display extra degradation steps that may be due to the presence of organic cations (ODA) (Fig. 4.33). The weight loss of ODA-BT sample tends to increase with the presence of alkyl ammonium cations. This is evident at temperature below 200 °C that witnessed a weight lose of about 20%, that could be due to the desorption of water molecules. In the second stage between 300-500 °C, significant weight loss (43%) is attributed to the thermal degradation of ODA organo-surfactant. The third degradation stage occurred from 500 to 800 °C with a weight loss of 45% that is assigned to dehydroxylation of bentonite clay layers.
Figure 4.35 (A) TG curves and (B) DTG curves of un-modified BT and ODA-BT
The mass plots of the pure TGLP and composite resins (TGLP-BT and TGLP-ODA-BT) are presented in Figure 4.34A, whereas the corresponding derivative data (DTG) is provided in Figure 4.34B. The TGA profiles of pure TGLP exhibited a peak at 125 °C. This peak suggests that the maximum rate of weight loss occurred at this temperature. The thermal decomposition process of TGLP/clay composites almost showed similar thermal behavior with pure TGLP. However, in the presence of bentonite and organo-bentonite, the TG curves are shifted to lower temperatures, suggesting the declining in thermal stability of composites with the addition of clays compared to pure TGLP. In the TGLP/BT composites, the maximum degradation temperature (T_{max}) is 95 °C. It can be observed that, most of the weight loss (20%) of the polymer happened at this stage while the maximum degradation temperatures of TGLP/ODA-BT occurred at 80 °C with a weight loss of 21%.

This behavior of composites can be interpreted through several aspects including the non-uniform distribution in the polymer matrix because of using a high content of clay. On the other hand, this behavior generally is attributed to the catalytic action of the bentonite clays due to the presence of Lewis acidic sites on the edges of montmorillonite, created upon organic modifier degradation (Bellucci et al., 2007). Moreover, unmodified bentonite can be present on the surface or in the interlayer, as well as some adsorbed water that can be liberated almost at low temperatures, thus enhancing the polymer degradation. For the TGLP-ODA-BT composite, the presence of quaternary ammonium ions also contributes to composite degradation because they degrade within low temperatures.
Figure 4.36 (A) TG curves and (B) DTG curves of pure TGLP, TGLP-BT, and TGLP-ODA-BT
CHAPTER 5
CONCLUSIONS AND FUTURE STUDIES

5.1 Conclusions

This study highlights the application and potential of oil palm based lignins in the synthesis of green phenolic resins. Environment-friendly lignin/tannin based wood adhesives were studied, with the aim of preparing formaldehyde-free wood adhesives and to increase the proportion of renewable environmentally friendly materials in these wood adhesive formulations.

The treatment of oil palm empty fruit bunch (OPEFB) fibers with alkaline and alcoholic solvent is practically suitable for the delignification process. The delignification processes were conducted using Kraft and auto-catalyzed ethanol–water pulping processes.

Characterization data showed that the organosolv lignin has higher syringyl (S) and guaiacyl (G) contents while the Kraft lignin has higher guaiacyl (G) content. Mannich reactivity analysis showed that Kraft lignin has higher amounts of activated free aromatic ring positions, which indicates more favorable reactions with the glyoxal compared to organosolv lignin. The molecular weight distribution ($M_n$, $M_w$, and polydispersity) of Kraft lignin is higher than organosolv lignin, due to the repolymerization reaction of Kraft lignin during the pulping process. TGA analysis indicated that Kraft lignin has higher thermal stability than organosolv lignin, which supports the hypothesis of using Kraft lignin in the applications of phenolic resins within a wide range of temperatures.
In order to improve lignin properties in the wood adhesives formulation, the preparation of lignin polyols was successfully achieved by using two methods, namely, the liquefaction of oil palm empty fruit bunch and of lignin with polyhydric alcohols and propylene oxide. Viscous lignin polyols were successfully characterized using FTIR, $^1$H and $^{13}$C NMR spectroscopy and GPC. Quantitative $^{13}$C NMR showed that all aliphatic hydroxyl group values of polyols significantly increased with the use of the two methods compared with lignin. The average molecular weight analysis of polyol products exhibited high molecular weight compared to lignin, indicating that condensation reactions have occurred between the Kraft lignin and multifunctional alcohols and incorporation of the aliphatic PEG and glycerol moieties into the lignin structure, which is a major confirmation towards the successful preparation of targeted lignin polyol products.

Tannin- glyoxalated Kraft lignin (TGKL) resin has a poor water resistance. To overcome this obstacle, this research was focused on the scalable adhesive through the modification of tannin adhesives and oligomeric precursors of a hyperbranched poly (amine-ester) (HBPAE). Hyperbranched poly (amine-ester) was prepared via pseudo-one-step process and was used in the modification of tannin adhesive during the synthesis steps of TGKL resins. FTIR, $^1$HNMR and $^{13}$CNMR spectra confirmed the successful preparation of HBPAE and MTGKL.

The water resistance of plywood specimens with MTGKL resin showed more superior properties than TGKL. After soaking and treatment of MTGKL plywood specimens in the tap water for 24 hours at room temperature, no delamination occurred in any of the specimens while delamination of plywood specimens with TGKL resin was observed, indicating the lack of water resistance for TGKL resin.
when it was used to bond plywood. This is due to the success of poly (amine-ester) in boosting the tannin structure via the reaction of the terminal units of glutaraldehyde with the hydroxyl groups of tannin and with –NH$_2$, -COOH, which led to the increase in the cross-linking density within the resin in the hot press process. The tensile strengths of MTGKL, both dry and wet are higher compared to TGKL resin with values of 39.72 and 27.62 MPa, respectively.

In this work, it was demonstrated that a combination of lignin polyols-tannin (TGLP) and polyethylenimine (PEI) was an excellent alternative for marine adhesive protein (MAP). The results revealed that the increase in PEI ratio led to an increase of the solid content of TGLP-PEI adhesives. The TGLP adhesives had poor water resistance compared with TGLP-PEI adhesive despite the high tensile strength (31.1 MPa). This is clearly shown when soaking the plywood specimens in the tap water and boiling water, where delamination occurred. However, at 10% of PEI with TGLP resin, the delamination of plywood specimens did not occur. All three tensile strengths (dry, WSAD, and BWT/dry) significantly increased when the weight ratio of the PEI increased from 10 to 20% compared with TGLP and CPF resins. These findings could be due to further reactions between the amino groups in the PEI with catechol moieties in both lignin and tannin, resulting in increased amounts of crosslinking linkages in the resin and therefore the tensile strength and water resistance increased, as well as, become more heat-resistant ($T_{\text{max}}$ 360 °C).

In this work, mixture of polyethylene glycol and glycerol as a liquefaction solvent and by glyoxal as curing agent used in the synthesis of resol resins from liquefaction of OPEFB in combination with tannin adhesive. The resol type liquefied wood/glyoxal/tannin (TGLW) resin showed a similar FTIR spectrum to that of CPF
resin. FTIR spectrum confirmed the reaction between liquefied OPEFB and glyoxal through the peaks of C-C, C-O, and C-O groups in the resol structure.

Interestingly, tensile strength values of TGLW surpassed the minimum requirement of the relevant international standard as per British Standard for dry tensile strength of plywood (≥0.35 MPa) and JIS K-6852 standard (i.e., 1.2 MPa). When soaking plywood specimens in the tap water for 24 hours at room temperature, no delamination occurred in any of the specimens.

There are not a lot of studies conducted on the influence of clays on wood adhesives prepared from biomass. The mechanical and thermal characteristics of TGLP system were studied. Modification of bentonite clay was implemented using octadecylamine (ODA) salt. FTIR, XRD, and SEM characterizations indicated that the modification of bentonite had occurred. The diffraction peaks of ODA-BT in the XRD pattern had shifted to lower angle (2θ = 4.8) with a basal spacing of 18.5 nm. These results demonstrated that the layer silicates galleries of the BT were expanded because of the modification of surfactants and intercalation of a long-chain of alkyl ammonium cation groups in a silicate layer of BT. The XRD pattern also confirmed the successful insertion of TGLP resin into the organo bentonite galleries as shown by the significant increase of basal spacing of TGLP-ODA-BT (18.99 nm) compared with TGLP-BT (6.2 nm).

The mechanical properties (tensile strengths) of TGLP composites have been considerably improved by incorporating both BT and ODA-BT. The tensile strengths revealed that the use of low contents of clay is better than using high clay content that could be due to the decrease in dispersion at high contents of clay. These results are particularly clear when using modified bentonite with ODA. This is probably due
to the decrease of some silicate layers in the ODA-BT compared with BT. Important characterizations of various samples are summarized in Table 5.1.
Table 5.1: Summary of significant results obtained

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
<th>DTG$_{max}$ °C</th>
<th>Tg °C</th>
<th>Solid content, %</th>
<th>Gel time, s</th>
<th>Tensile strength MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Dry</td>
</tr>
<tr>
<td>KL</td>
<td>1564</td>
<td>2.62</td>
<td>380</td>
<td>154.89</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>AEL</td>
<td>1231</td>
<td>1.83</td>
<td>360</td>
<td>118.50</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Liquefied KL</td>
<td>16730</td>
<td>13.94</td>
<td>400</td>
<td>37.25</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Liquefied OBEFB</td>
<td>12203</td>
<td>11.40</td>
<td>380</td>
<td>38.54</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>KL-PO</td>
<td>2566</td>
<td>3.52</td>
<td>180</td>
<td>41.98</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>TGKL</td>
<td>----</td>
<td>----</td>
<td>220</td>
<td>----</td>
<td>39.26</td>
<td>164</td>
<td>28.79</td>
</tr>
<tr>
<td>MTGKL</td>
<td>----</td>
<td>----</td>
<td>310</td>
<td>----</td>
<td>53.08</td>
<td>235</td>
<td>39.72</td>
</tr>
<tr>
<td>TGLP</td>
<td>----</td>
<td>----</td>
<td>225</td>
<td>----</td>
<td>45.82</td>
<td>160</td>
<td>31.16</td>
</tr>
<tr>
<td>TGLP-20% PEI</td>
<td>360</td>
<td></td>
<td></td>
<td>56.92</td>
<td>101.22</td>
<td>63.04</td>
<td>59.48</td>
</tr>
<tr>
<td>TGLW</td>
<td>----</td>
<td>----</td>
<td>360</td>
<td>----</td>
<td>43.8</td>
<td>204</td>
<td>21.40</td>
</tr>
<tr>
<td>TGLP-4% BT</td>
<td>----</td>
<td>----</td>
<td>95</td>
<td>----</td>
<td>----</td>
<td>35.89</td>
<td>----</td>
</tr>
<tr>
<td>TGLP-3% ODA-BT</td>
<td>----</td>
<td>----</td>
<td>80</td>
<td>----</td>
<td>----</td>
<td>44.92</td>
<td>----</td>
</tr>
<tr>
<td>CFP</td>
<td>----</td>
<td>----</td>
<td>380</td>
<td>59.80</td>
<td>480</td>
<td>1.39</td>
<td>1.25</td>
</tr>
</tbody>
</table>
5.2 Future Studies

1. Extraction of lignin from oil palm empty fruit bunch by various of delignification processes such as soda pulping, microwave extraction, pyrolysis or gasification, enzymatic hydrolysis to give better yields and properties could be studied.

2. The applications of lignin as phenolic resins should be further explored with specific properties to suit the different temperatures during the hot press in order to convince the wood industry to substitute lignin for phenol.

3. There are many curing reagents that can be used as cross-linker of lignin-based adhesive, such as aldehyde. Besides glyoxal, other non-toxic and non-volatile chemical reagents, such as furfural and glutaraldehyde could be used to cross-link lignin molecular. Its mechanism and preparing procedure deserved to be studied.

4. Liquefaction process of lignin incorporation with tannin adhesive need to be explored in order to determine the influence of liquefaction process on the properties of lignin and the resulting adhesives.

5. It is well known that the tannic acid is cheaper than tannin and thus the economic feasibility of the preparation of adhesives will be better.

6. Many traditional modification processes have been used to improve lignin properties as wood adhesives. In the preparation of biomass based-adhesive future work should focus on the study of modification processes both on
lignin and tannin to prepare thermally stable water resistant adhesives comparable to commercial phenol formaldehyde resin.

7. Preparation of wood adhesives from liquefied wood can be developed to prepare water resistant adhesives in hot or boiling water.

8. Intercalation/ or exfoliation of the clay in lignin adhesive matrix need more understanding. Other kinds of clay could be developed to obtain water resistant wood adhesives.
REFERENCES


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Van Langenberg, K., Grigsby, W., Ryan, G., 2010. Green adhesives : options for the australian industry – summary of recent research into green adhesives from renewable materials and identification of those that are closest to commercial uptake. For. Wood Prod. Aust. 61, 10–16.


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APPENDIX I. FTIR, $^{13}$CNMR, $^1$H NMR of lignin samples

Table 1. FTIR absorption bands and assignments for Kraft and organosolv lignin.

<table>
<thead>
<tr>
<th>Band (cm$^{-1}$)</th>
<th>assignments</th>
<th>KL Band location (cm$^{-1}$)</th>
<th>AEL Band location (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400–3405</td>
<td>O–H stretching (phenolic OH and aliphatic OH)</td>
<td>3407</td>
<td>3404</td>
</tr>
<tr>
<td>2960–2925</td>
<td>C–H stretching (CH$_3$ and CH$_2$ groups)</td>
<td>2936</td>
<td>2941.5</td>
</tr>
<tr>
<td>2850–2840</td>
<td>C–H stretching (OCH$_3$)</td>
<td>2844.5</td>
<td>2844.8</td>
</tr>
<tr>
<td>1705–1715</td>
<td>C=O stretching (unconjugated ketone, carbonyl and ester groups)</td>
<td>1705.7</td>
<td>1707</td>
</tr>
<tr>
<td>~1600</td>
<td>C–C stretching (aromatic skeleton)</td>
<td>1597</td>
<td>1594</td>
</tr>
<tr>
<td>1513</td>
<td>C–C stretching (aromatic skeleton)</td>
<td>1512.7</td>
<td>1512.5</td>
</tr>
<tr>
<td>1460</td>
<td>C–H deformation (asymmetric in –CH$_3$ and –CH$_2$)</td>
<td>1452.4</td>
<td>1454.7</td>
</tr>
<tr>
<td>1425</td>
<td>C–C stretching (aromatic skeleton) with C–H in-plane deformation</td>
<td>1425.9</td>
<td>1423.6</td>
</tr>
<tr>
<td>1326</td>
<td>C–O stretching (S)</td>
<td>disappeared</td>
<td>1324.8</td>
</tr>
<tr>
<td>~1220</td>
<td>C–O(H) + C–O(Ar) (phenolic OH and ether in S and S)</td>
<td>1207.6</td>
<td>1214.4</td>
</tr>
<tr>
<td>1115</td>
<td>Ar–CH in plane deformation (S)</td>
<td>1113</td>
<td>1118.4</td>
</tr>
<tr>
<td>~1030</td>
<td>C–O(H) + C–O(C) (first order aliphatic OH and ether)</td>
<td>1030.3</td>
<td>1033</td>
</tr>
<tr>
<td>915</td>
<td>C–H out of plane (aromatic ring)</td>
<td>913</td>
<td>916</td>
</tr>
<tr>
<td>854</td>
<td>C–H out of plane vibrations in position 2, 5 and 6 of S units</td>
<td>849.5</td>
<td>851.6</td>
</tr>
<tr>
<td>817</td>
<td>C–H out of plane vibrations in position 2, 5 and 6 of G units</td>
<td>816.1</td>
<td>819</td>
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</table>
Table 2. Chemical shift value (δ, ppm) of $^{13}$C-NMR spectrum of acetylated lignin samples.

<table>
<thead>
<tr>
<th>(δ, ppm)</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>172.4- 170</td>
<td>OCOCH$_3$</td>
</tr>
<tr>
<td>168.5</td>
<td>Cγ, p-coumaryl ester</td>
</tr>
<tr>
<td>152.5</td>
<td>C-2/C6, C-4 and C-3/C5, syringyl</td>
</tr>
<tr>
<td>145</td>
<td>C-2, C-6, guaiacyl etherified</td>
</tr>
<tr>
<td>139.5</td>
<td>C-4, syringyl</td>
</tr>
<tr>
<td>136.5</td>
<td>C-1, guaiacyl etherified</td>
</tr>
<tr>
<td>131</td>
<td>C2/C6, p-coumaryl ester</td>
</tr>
<tr>
<td>127.4 and 128.6</td>
<td>C2/C6, p-Hydroxyphenyl</td>
</tr>
<tr>
<td>124.7</td>
<td>C1, p-coumaryl ester</td>
</tr>
<tr>
<td>118.4</td>
<td>C3/C5, p-coumaryl ester</td>
</tr>
<tr>
<td>104</td>
<td>C-4</td>
</tr>
<tr>
<td>81.5</td>
<td>Cβ in S β–O–4 erythro</td>
</tr>
<tr>
<td>72</td>
<td>Cα in β–O–4 G and S erythro</td>
</tr>
<tr>
<td>64</td>
<td>Cγ with Cα= O, Cγ–O p-coumaryl ester</td>
</tr>
<tr>
<td>60.3</td>
<td>Cγ in β–O–4 G and S threo and erythro</td>
</tr>
<tr>
<td>56.3</td>
<td>OCH$_3$ in G and S</td>
</tr>
<tr>
<td>31.7 and 29.4</td>
<td>α and β methylene groups</td>
</tr>
<tr>
<td>21</td>
<td>CH$_3$ in the acetyl groups</td>
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<tr>
<td>15.5 and 14.4</td>
<td>Methylene in n-propyl side chain</td>
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</table>
Table 3. Signal assignment for $^1$H NMR spectrometry of acetylated lignin samples

<table>
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<th>Signal (ppm)</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>7.5-6.5</td>
<td>Aromatic H in S and G units</td>
</tr>
<tr>
<td>7.4</td>
<td>Aromatic H in G</td>
</tr>
<tr>
<td>6.8</td>
<td>Aromatic H in S</td>
</tr>
<tr>
<td>3.1-4.0</td>
<td>Methoxyl H</td>
</tr>
<tr>
<td>2.2-2.5</td>
<td>H in aromatic acetates</td>
</tr>
<tr>
<td>2.2-1.8</td>
<td>H in aliphatic acetates</td>
</tr>
<tr>
<td>1.5-0.8</td>
<td>Aliphatic H</td>
</tr>
</tbody>
</table>
APPENDIX II. GPC analysis of lignin and lignin polyols samples

Figure 1. Weight average ($M_w$) (gmol$^{-1}$) and number average ($M_n$) (gmol$^{-1}$) of KL.

Figure 2. Weight average ($M_w$, gmol$^{-1}$) and number average ($M_n$, gmol$^{-1}$) of AEL.
Figure 3. Weight average ($M_w$, g mol$^{-1}$) and number average ($M_n$, g mol$^{-1}$) of liquefied KL with PEG/ GLY.

Figure 4. Weight average ($M_w$, g mol$^{-1}$) and number average ($M_n$, g mol$^{-1}$) of liquefied OPEFB with PEG/ GLY.
Figure 5. Weight average ($M_w$, gmol$^{-1}$) and number average ($M_n$, gmol$^{-1}$) of liquefied KL with PO.
APPENDIX III. DSC of lignin and lignin polyols samples.

Figure 1. DSC heating curves of KL.

Figure 2. DSC heating curves of AEL.
Figure 3. DSC heating curves of liquefied KL with PEG/ GLY.

Figure 4. DSC heating curves of liquefied OPEFB with PEG/ GLY.
Figure 5. DSC heating curves of liquefied KL with PO.
APPENDIX IV. Tensile strength, elastic modulus and elongation@break of plywood using various wood adhesives

Figure 1. Tensile strength (dry), elastic modulus and elongation@break of plywood using TGKL resin.

Figure 2. Tensile strength (dry), elastic modulus and elongation@break of plywood using MTGKL resin.
Figure 3. Tensile strength, elastic modulus and elongation@break of plywood using MTGKL resin in tap water for 24 h.

Figure 4. Tensile strength (dry), elastic modulus and elongation@break of plywood using CPF resin.
Figure 5. Tensile strength, elastic modulus and elongation@break of plywood using CPF resin in tap water for 24 h.

Figure 6. Tensile strength, elastic modulus and elongation@break of plywood using CPF resin in boiling water for 2 h.
Figure 7. Tensile strength (dry), elastic modulus and elongation@break of plywood using TGLP resin.

Figure 8. Tensile strength (dry), elastic modulus and elongation@break of plywood using TGLP-PEI (10%) resin.
Figure 9. Tensile strength (dry), elastic modulus and elongation@break of plywood using TGLP-PEI (12%) resin.

Figure 10. Tensile strength (dry), elastic modulus and elongation@break of plywood using TGLP-PEI (14%) resin.
Figure 11. Tensile strength (dry), elastic modulus and elongation@break of plywood using TGLP-PEI (16%) resin.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>Max. Load (N)</th>
<th>Tensile Strength (MPa)</th>
<th>Elastic Modulus (MPa)</th>
<th>Elongation@break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.000</td>
<td>5.000</td>
<td>5921.664</td>
<td>47.373</td>
<td>322.636</td>
<td>17.235</td>
</tr>
</tbody>
</table>

Figure 12. Tensile strength (dry), elastic modulus and elongation@break of plywood using TGLP-PEI (18%) resin.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>Max. Load (N)</th>
<th>Tensile Strength (MPa)</th>
<th>Elastic Modulus (MPa)</th>
<th>Elongation@break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.000</td>
<td>5.500</td>
<td>7156.809</td>
<td>54.218</td>
<td>300.374</td>
<td>21.311</td>
</tr>
</tbody>
</table>
Figure 13. Tensile strength (dry), elastic modulus and elongation@break of plywood using TGLP-PEI (20%) resin

Figure 14. Tensile strength, elastic modulus and elongation@break of plywood using TGLP-PEI (10% PEI) resin in tap water for 24 h.
Figure 15. Tensile strength, elastic modulus and elongation@break of plywood using TGLP-PEI (12% PEI) resin in tap water for 24 h.

Figure 16. Tensile strength, elastic modulus and elongation@break of plywood using TGLP-PEI (14% PEI) resin in tap water for 24 h.
Figure 17. Tensile strength, elastic modulus and elongation@break of plywood using TGLP-PEI (16% PEI) resin in tap water for 24 h.

Figure 18. Tensile strength, elastic modulus and elongation@break of plywood using TGLP-PEI (18% PEI) resin in tap water for 24 h.
Figure 19. Tensile strength, elastic modulus and elongation@break of plywood using TGLP-PEI (20% PEI) resin in tap water for 24 h.

Figure 20. Tensile strength, elastic modulus and elongation@break of plywood using TGLP-PEI (10% PEI) resin in boiling water for 2 h.
Figure 21. Tensile strength, elastic modulus and elongation@break of plywood using TGLP-PEI (12% PEI) resin in boiling water for 2 h.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>Max. Load (N)</th>
<th>Tensile Strength (MPa)</th>
<th>Elastic modulus (MPa)</th>
<th>Elongation@break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.500</td>
<td>5.600</td>
<td>3730.609</td>
<td>30.454</td>
<td>283372</td>
<td>14.663</td>
</tr>
</tbody>
</table>

Figure 22. Tensile strength, elastic modulus and elongation@break of plywood using TGLP-PEI (14% PEI) resin in boiling water for 2 h.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>Max. Load (N)</th>
<th>Tensile Strength (MPa)</th>
<th>Elastic modulus (MPa)</th>
<th>Elongation@break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>5.100</td>
<td>3932.633</td>
<td>32.813</td>
<td>192.949</td>
<td>28.318</td>
</tr>
</tbody>
</table>
Figure 23. Tensile strength, elastic modulus and elongation@break of plywood using TGLP-PEI (16% PEI) resin in boiling water for 2 h.

Figure 24. Tensile strength, elastic modulus and elongation@break of plywood using TGLP-PEI (18% PEI) resin in boiling water for 2 h.
Figure 25. Tensile strength, elastic modulus and elongation@break of plywood using TGLP-PEI (20% PEI) resin in boiling water for 2 h.

Figure 26. Tensile strength (dry), elastic modulus and elongation@break of plywood using TGLW resin.
Figure 27. Tensile strength, elastic modulus and elongation@break of plywood using TGLW resin in tap water for 24 h.
APPENDIX V. EDX Elemental analysis of un-modified bentonite, modified bentonite, and composites

1. EDX Elemental analysis of unmodified BT.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Compd %</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>12.79</td>
<td>18.28</td>
<td>46.85</td>
<td>CO2</td>
</tr>
<tr>
<td>Mg K</td>
<td>1.73</td>
<td>1.23</td>
<td>2.88</td>
<td>MgO</td>
</tr>
<tr>
<td>Al K</td>
<td>5.73</td>
<td>3.65</td>
<td>10.82</td>
<td>Al2O3</td>
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<tr>
<td>Si K</td>
<td>17.96</td>
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<tr>
<td>Ca K</td>
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<td>0.32</td>
<td>1.03</td>
<td>CaO</td>
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<tr>
<td>O</td>
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<td>65.55</td>
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<td>Totals</td>
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</table>

2. EDX Elemental analysis of ODA-BT.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Compd %</th>
<th>Formula</th>
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</thead>
<tbody>
<tr>
<td>C K</td>
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<td>77.37</td>
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<tr>
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<td>0.44</td>
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<tr>
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<td>Al2O3</td>
</tr>
<tr>
<td>Si K</td>
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<td>3.43</td>
<td>13.31</td>
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<tr>
<td>O</td>
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<tr>
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</table>
3. EDX Elemental analysis of TGLP- BT resin.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
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<th>Compd %</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
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<td>3.54</td>
<td>7.11</td>
<td>Na2O</td>
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<tr>
<td>Al K</td>
<td>1.21</td>
<td>0.69</td>
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<td>Si K</td>
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<tr>
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</tr>
</tbody>
</table>

4. EDX Elemental analysis of TGLP- ODA-BT resin.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
<th>Compd %</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>Al K</td>
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<td>0.36</td>
<td>1.21</td>
<td>Al2O3</td>
</tr>
<tr>
<td>Si K</td>
<td>0.72</td>
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