Synthesis and characterization of biomass derived bio-epoxy resins.

(バイオマス由来バイオエポキシ樹脂の合成と機能性評価)

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Abstract

Increasing industrialization has caused sudden rise in energy consumption. Traditional methods of energy production being based on fossil fuels like oil and gas, have resulted in the emission of excess greenhouse gasses (CO_2), which is the main cause for the climactic changes. The climate change (especially temperature rise) could lead the glacier to melt, causing the raise in ocean level subsequently, endangering the existence of plants and animals. Hence, to reduce these kind of environmental issues, an immediate action should be taken to discourage the consumption of fossil fuels, by encouraging the use of renewable plant biomasses. Biomass is one of the most promising alternative energy sources, because of their carbon neutrality and availability from multiple sources.

In the effort to search the different biomass resources for the synthesis of epoxy resins, the renewable resources like green tea extract, lignin extracted from different woody biomasses i.e., eucalyptus, bamboo, and cedar were extensively studied in this thesis work.

The active ingredients of Japanese green tea (*Camellia sinensis*) were utilized to synthesize bio-based epoxy resin. The catechin compounds in the aqueous extract of green tea were functionalized with epichlorohydrin under alkaline conditions in the presence of tetramethylammonium chloride (TMAC), a water soluble phase transfer catalyst. A good yield of resin was synthesized, and curing was performed with methanol soluble lignin extracted from eucalyptus. The epoxy networks, so synthesized, were compared with bisphenol-A (BPA)-derived epoxy network.

The thermal and mechanical properties of the bio-based resin were assessed through thermogravimetric, flexural strength, and glass transition (Tg) analyses. Catechin-based epoxy networks were found to exhibit good thermal and mechanical properties, rendering them potential BPA substitutes. The thermal decomposition temperature resulting in 5% weight loss (Td_5) of synthesized epoxy resin was found to be above 300 °C, which is slightly lower than that of BPA-derived epoxy resin. The synthesized bio-based resins meet the requirement for the dip-solder resistant temperature (250–280 °C), with Tg values ranging from 155 to 178 °C, highlighting their potential use as one of the most suitable BPA substituents as well as their use in electronic materials.

Likewise, a low molecular weight lignin from various lignocellulosic materials was used for the synthesis of bio-based epoxy resins. The lignin extracted with methanol from steam-exploded samples (steaming time of 5 min at steam pressure of 3.5 MPa) from different biomasses (i.e., cedar, eucalyptus, and bamboo) were functionalized by the reaction with epichlorohydrin, catalyzed by a water-soluble phase transfer catalyst tetramethyl ammonium chloride (TMAC), which was subsequently reacted with aqueous NaOH (30 Wt.%) for ring closure using methyl ethyl ketone as a solvent. The glycidylated products of the lignin with good yields were cured to epoxy polymer networks with bio-based curing agents i.e., lignin itself and a commercial curing agent TD2131. Relatively good thermal properties of the bio-based epoxy network were obtained over commercially available bisphenol A (BPA) based epoxy resin. Among the epoxy resins synthesized from three different biomasses, cedar-derived epoxy resin showed the higher thermal decomposition

temperature at 5% weight loss (Td_5) than those derived from eucalyptus and bamboo, respectively.

However, all the synthesized bio-based resins satisfy the stability requirement temperature, which is between 250-280 °C, rendering their applicability in the field of electronics (especially in circuit boards). Besides that, the methanol-insoluble residues were enzymatically hydrolyzed to produce glucose, which is one of the major precursors in the field of bio-ethanol fermentation. This study indicated that the biomass-derived methanol-soluble lignin could be e a promising candidate to be used as a substitute for petroleum-based epoxy resin derived from BPA, while insoluble residues could be utilized to obtain a bio-ethanol precursor i.e., glucose.

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Chapter 1

Introduction

Epoxy-based polymer materials have wide spread applications ranging from printed circuit boards, semiconductor encapsulants, metal coatings, automotive primers, adhesives, aerospace, composite materials, reinforcing composite materials, to even as building materials for rotor blades of wind turbines. Apart from industrial applications, epoxy resins have their application in human health sector such as filling materials or sealants in dentistry. The epoxy resin market is faced with an ever increasing demand of high performance epoxy resin.

The epoxy resins or thermosetting materials have a set of unique properties, which are generally not found in other plastic materials, such as good thermal stability and excellent mechanical strength, outstanding chemical, moisture and corrosion resistance, good adhesive, and electrical properties. One more important features of the epoxy resin is having dimensional stability or low shrinkage upon curing, and also a low emissions of volatiles.

A most common route to the commercial epoxy resins is from reacting epichlorohydrin (ECH) with bisphenol A (BPA) to give glycidyl ethers of BPA (GEBPA). The low molecular weight and rigid aromatic ring with reactive hydroxyl functional groups of BPA leads to the epoxy resins with higher performance and versatile applications. However, BPA is a fossil fuel based substrate with volatile price and limited resource because of its rapid depletion. Besides, BPA has been

listed as carcinogenic, mutagenic, and reprotoxic (CMR) (Nouailhas et. al., 2011), and hence its use has been strictly limited in the countries like Canada and France. So, the current emphasis of the researchers in the field of resin synthesis should be focused on renewable resources, or in the other words, BPA resource should be switched to renewable resource.

Recently, biomass has been increasingly popular as a renewable energy resource. Since last few decades, several studies have been conducted focusing on the utilization of renewable resource as a raw material. Biomass is considered to be one of the best promising resources of present and future because of its renewability, abundant availability, followed by its biodegradability. Lignin being one of the most important commodity of biomass, is also precursor to the aromatic compounds, which are the route to the important class of medicinal compounds as well. The reactivity of the biomass substrate is determined by their particular structures with specific functional groups. Lignin has phenolic and aliphatic hydroxyl groups, which have enabled their utilization as a substitute to bisphenol A (BPA).

Tremendous amount of researches have been conducted to find the suitable substitute to BPA. oils (Crivello et al., 1997; Goud et al., 2006, 2007; Vlcek and Petrovic, 2006), green tea catechins (Benyahya et al., 2014; Basnet et al., 2015), liquidified wood (Kishi et al., 2011), lignin (Sasaki et al., 2013), tung oil fatty acids, rosin diacid, dimerized fatty acid (Huang et al., 2013a,b), cinnamic acid, dipentene (Xin et al., 2014), eugenol, rosin (Qin et al., 2014; Liu and Zhang, 2010), pine bark extractives (Kuo et al., 2014) have been identified as potential bio resources for the synthesis of bio-based epoxy resin.

This present thesis reports about the possibility of utilizing different biomass as a substrate of epoxy resin synthesis. The synthesis of the thermosetting resins were conducted with biomass derived extractives and the characterization of the synthesized resins was conducted. The organic solvent soluble; low molecular weight extractives extracted from Japanese green tea (*Camellia sinensis*) and lignin extracted from steam exploded woody biomass i.e. eucalyptus, bamboo, and cedar were employed as a substrate to synthesize epoxy resins.

The water soluble extractives from green tea was extracted with hot distilled water (DW) at 80 °C, followed by the vacuum evaporation/freeze drying , then was subsequently extracted with organic solvent (methanol), in order to extract low molecular weight lignin, followed by the subsequent partition with DW/chloroform/ethyl acetate (EA) for the further purification. The significant amount (8% of the total substrate employed for the extraction) of EA soluble extractives were obtained through overall extraction and purification steps. The EA purified as well as methanol extracted samples were employed, separately to synthesize epoxy resins and the effect of purification and the sample extraction technique on the overall properties of synthesized resins.

In case of woody biomass, i.e. eucalyptus, bamboo, and cedar, steam explosion was applied to carry out the pretreatment. The purpose of this pretreatment is to break down the shield formed by lignin, increase the available surface area, disrupt the crystalline structure and reduce the degree of polymerization of cellulose in order to enhance enzyme accessibility to the cellulose during hydrolysis (Zheng et al. 2009; Mosier et al. 2005). The structure of the lignin is immensely complex and

forms a three dimensional network. The network is formed mainly by three types of monolignols that are linked together by different ether and carbon-carbon bonds. Lignin is the most abundant aromatic polymer in the nature, composed of phenyl propane units (Suhas et al. 2006), which make up 15-35% of wood and is present in the middle lamella as well as in the cell wall. Lignin provides cell wall a stiffness, subsequently providing mechanical strength to the tree. The other function of lignin is to protect the tree against microbial degradation and making the cell wall hydrophobic to give an efficient transportation system of water and nutrition (Suhas et al. 2006; Norberg 2012). Hence, the woody biomass were steam exploded in order to separate the complex lignin from cellulose and hemicellulose, to imply them further. The another main reason to choose steam explosion pretreatment in this study was to make the lignin more desirable substrate to synthesize epoxy resin which could be used in electronic field, especially in preparing circuit board.

Also, this study shows that the desired properties of the synthesized epoxy resins could be achieved through the careful selection of substrate and their extraction, followed by the purification, the proper curing agent, and the right epoxy/agent curing ratios during the epoxy resin formulation process. Hence, in this study, the synthesis of a catechin-based epoxy resin from green tea aqueous extract and steam exploded woody biomass have been described, and the possibility of curing the synthesized resins with natural curing agent, i.e., lignin extracted form *eucalyptus globulus* hard wood have been investigated.

Chapter 2

Synthesis and characterization of the green tea derived catechin-based epoxy resins.

2.1. INTRODUCTION

For the sustainable development of the economy and society, there is no better option over utilizing renewable resources. As a result, plant biomass has garnered a significant attention as a chemical resource for replacing fossil fuel resource. Molecular biomass such as vegetable oils (Lligadas et. al., 2013), lactic acid (Orozco et al., 2009), etc. have been engineered into renewable polymers. Utilizing renewable resources has number of benefits over fossil fuel based resources, such as reductions of carbon footprint and dependence on fossil fuels as organic material feedstock, production of biodegradable polymers which are biocompatible and environmentally benign. So, exploring the low toxic substituents, particularly from renewable resources to synthesize the novel epoxy polymers, which have comparable properties to BPA based epoxy resins, should be the major focus of researchers who have been working on the field of green chemistry.

Camellia sinensis (green tea) is a hydroxyl function rich renewable biomass. This molecular biomass contains catechin as a major compound. The feasibility of using catechin as an aromatic based substrate to synthesize epoxy resin is examined in this study. The distill water extracted catechin from *Camellia sinensis* was employed to synthesize bio-based epoxy resin by reacting with epichlorohydrin

under alkaline condition, followed by the curing of the synthesized resin with methanol soluble lignin extracted from Eucalyptus wood chips. The resultant combination of natural biomass and natural curing agents to synthesize epoxy resin displayed an interesting properties over BPA based resin. Hence, this study explored the potential of green tea extracted catechin as a one of the most suitable substituents to BPA.

2.2. MATERIALS AND METHODS

2.2.1. Chemicals

Green tea was purchased from the local market of Tokushima city, Japan. Lignin was extracted from steam exploded eucalyptus wood chips. All chemicals used in this experiments were purchased from commercial sources and employed without further purification. Epichlorohydrin (ECH), tetramethylammonium chloride (TMAC), sodium hydroxide (NaOH), dimethyl sulfoxide-d_6(DMSO), ethyl acetate (EA), chloroform (CHCl$_3$), tetrahydrofuran (THF), methanol (MeOH), hydrochloric acid (HCL), and standard catechin compound were purchased from Wako pure chemicals, Japan and were used without further purification.

2.2.2. Extraction of catechin from green tea sample

The purchased green tea was extracted with distilled water (DW). Crudely crushed (2×0.1 cm) green tea leaves were weighed, and 75 g extracted with 3 L of preheated DW in a 3 L volumetric flask at 60 °C for 20 min with continuous stirring (Koike precision instruments, magnetic stirrer model Heracles 20G, Japan) at a speed of 7. The aqueous extract was allowed to cool down to room temperature, filtered for the removal of tea residue, transferred to three evaporating flasks each of 1 L capacity, and stored overnight at -70 °C. For 14 days from the following day, the extracts were subjected to freeze drying to ensure complete evaporation of the solvent; freeze-dried green tea extract (FDGTE) was thereby obtained . Samples for heat drying were also similarly obtained; 3 L of extracts were evaporated under conditions of reduced pressure at 80 °C to obtain heat dried green tea extract (HDGTE). The evaporated samples obtained from both processes were powdered using mortar and pestle, weighed to determine yield, and employed in subsequent experiments.

2.2.3. Purification and removal of caffeine from the DW-extractives

The powdered samples were then re-suspended in 400 mL of DW, and partitioning was carried out by the addition of 400 mL of chloroform. After vigorous shaking, the suspension was left overnight for complete transfer of caffeine into chloroform portion, followed by removal of the chloroform portion and evaporation to dryness. This process was repeated thrice to achieve complete removal of caffeine. The aqueous portion left out after the removal of chloroform portion was further partitioned by the addition of 400 mL of ethyl acetate, followed by vigorous shaking

and standing overnight. Ethyl-acetate is well characterized solvent for the efficient extraction of flavonoid compounds, and was thereby employed for the recovery of catechins from the aqueous portion. The ethyl acetate portion was subsequently transferred to an evaporating flasks, and evaporated to dryness. This step was repeated thrice to allow complete recovery of catechin from the aqueous portion. The catechin so obtained was employed in subsequent experiments.

2.2.4. Determination of hydroxyl equivalent weight

The hydroxyl equivalent weight of the extracted catechin was determined using acetic anhydride-pyridine method. Ethyl acetate (40 mL), perchloric acid (0.4 g), and acetic anhydride (0.8 mL) were mixed in a vial, covered with aluminum foil, and kept at room temperature. Likewise, 4.2 mL of acetic anhydride was refrigerated at 5 °C for 30 min, followed by mixing with the aforementioned solution (maintained at room temperature), refrigerating further 1 h at 5 °C, and subsequently brought back to room temperature (solution A). Similarly, 30 mL of pyridine was mixed with 10 mL of DW in a vial (solution B). A 0.5 M solution of ethanolic potassium hydroxide (KOH-EtOH) solution collected in a burette was employed for volumetric titration.

Solution A (10 mL) was added to the samples (0.5 g), followed by stirring for 15 min. Solution B (2 mL) was then added, followed by further stirring for 5 min. This was followed by the addition of pyridine (10 mL) and titration with 0.5 M solution of KOH-EtOH. The resulting millivoltage (mV) was recorded and employed for generating a graph for calculating the volume of titrant consumed. The same

conditions were employed for the blank assay but in the absence of catechin. The difference in the volume of titrant consumed by the blank and catechin titrations represents the amount of acetic acid consumption of the sample and consequently, the content of free hydroxyl group in the green tea extract catechin. The number of free hydroxyl groups was calculated using equation 1:

$$[OH] = \frac{\text{Blank (mL)} - \text{Sample (mL)} \times F \times 28.05}{\text{sample (g)}} \ldots\ldots\ldots\ldots (1),$$

where F is the factor for KOH-EtOH solution provided by the manufacturer.

The acid value was determined by the addition of acetone (30 mL) to the green tea sample (1 g), followed by the titration with KOH-EtOH solution. The resulting mV and pH were recorded and employed for generating a graph for calculating the volume of titrant consumed. The experiment was conducted in duplicate, and the average value was used. The acid value was calculated using equation 2:

$$[O] = \frac{\text{KOH} - \text{EtOH (mL)} \times F \times 28.05}{\text{sample (g)}} \ldots\ldots\ldots\ldots (2),$$

where F is the factor for KOH-EtOH solution provided by the manufacturer.

Finally, the hydroxyl equivalent weight was calculated using equation 3:

$$[OH] = \frac{56.1 \times 1000}{[OH] + [O]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

2.2.5. Extraction of lignin as a natural curing agent

The wood chips of eucalyptus (1-3 cm wide) were employed for the extraction of lignin. A steam explosion apparatus equipped with a reactor of 2 l capacity (Steam explosion apparatus NK-2 L, Japan Chemical Engineering and Machinery Co. Ltd, Osaka, Japan) was employed for steam explosion of the wood chips. The sample (200 g) was introduced into the reactor and exposed to the saturated steam at 3.5 MPa (243 °C) for a steaming time of 5 min. Following this step, a ball valve at the bottom of the reactor was abruptly opened in order to rapidly reduce the pressure of the reactor to atmospheric pressure, generating a steam-exploded product of liquid-solid materials in the receiver. The moisture content of the steam exploded wood chips was determined, and water-soluble lignin was extracted with DW by continuous stirring at room temperature for 24 h. Following the removal of water-soluble lignin, the residue was further extracted with methanol (MeOH) in order to obtain methanol soluble-lignin (Fig. 1). The methanol-soluble lignin so obtained was employed as a natural curing agent for synthesized catechin-based epoxy resin.

2.2.6. Synthesis of green tea catechin based epoxy resin

Epoxidation in general is of commercial importance due to the high reactivity of the functional group from substrate, allowing its ready transformation into other important functional and polymerizable groups. ECH is widely employed in the

synthesis of epoxy polymers, and was therefore also used for the synthesis of green tea catechin-based epoxy polymer. Catechin was treated under alkaline conditions with ECH in the presence of TMAC, as a water soluble phase transfer catalyst (Fig. 2). Four grams of green tea extract or standard catechin was taken in a four-necked 1 L flask equipped with an efficient stirrer, condenser and a septum cap, and solubilized in 15 mL of ethanol due to the insolubility of catechin in ECH. This was followed by the addition of ECH (303 g); the amount of ECH was calculated on the basis of free hydroxyl group content in the green tea sample (determined by the acetic anhydride and pyridine method), as tabulated in Table 1. The reaction was carried out under nitrogen flow in an oil bath at 90 °C with continuous stirring (at 250 rpm). After 10 min, an aqueous solution of TMAC (1 mol/OH) was added drop wise, and further continued for 1.5 h under the same conditions of temperature and nitrogen flow.

TMAC is the phase transfer catalyst, and catalyzes the reaction allowing to open epoxy ring, resulting the release of hydrogen chloride. Thereafter, the temperature of the reaction was gradually reduced to room temperature over the duration of 1 h. The epoxy ring was reconstructed by the drop-wise addition of concentrated sodium hydroxide solution (50%, w/v, in DW) over 5 min, followed by the further reaction for 2 h at room temperature to ensure completion of the reaction. The resulting suspension was then filtered and washed thrice with 100 mL of DW in order to remove salts generated as byproducts of the reaction as well as the residual catalyst. The organic layer was separated and evaporated to dryness under reduced

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pressure for the removal of excess ECH, and subjected to overnight drying at 40 °C in a vacuum oven to obtain the glycidyl product of catechin.

2.2.7. Determination of epoxy equivalent weight of the synthesized catechin-based resin

Epoxy equivalent weight (EEW) of the synthesized epoxy resin was determined using dioxane-hydrochloric acid method. A 0.12 N sodium hydroxide in methanol (NaOH-MeOH, 1.2 g of NaOH dissolved in 250 mL of MeOH) solution was prepared 1 day prior to the determination of EEW. The solution was stirred overnight at room temperature using a magnetic stirrer. A solution containing 4 mL of hydrochloric acid (HCl) and 246 mL of 1, 4-dioxane was prepared on the same day of titration. Volumetric titration was conducted with the NaOH-MeOH solution in the burette.

Methanol (25 mL) and HCl-dioxane (25 mL) were added to the synthesized resin (100 mg) collected in a 100 mL vial, followed by stirring for 15 min. Titration was conducted by the addition of NaOH-MeOH solution from burette. The resulting mV was recorded and employed for generating a graph for calculating the volume of titrant consumed. The blank assay was performed under the same condition but in the absence of sample. The experiment was conducted in duplicate, and the average value was used. The EEW of the synthesized resin was calculated using the equation 4:

$$EEW = \frac{10000 \times W \text{ (sample wt.)}}{F \text{ (Blank mL } - \text{sample mL)}} \cdots\cdots\cdots\cdots\cdots (4),$$

where F is the factor for NaOH-MeOH solution, which was calculated dividing the amount of NaOH used by 1.2.

2.2.8. Formulation of synthesized epoxy networks

The synthesized epoxy networks of glycidyl ether of HDGTE (GEHDGTE), glycidyl ether of FDGTE (GEFDGTE), glycidyl ether of standard catechin (GEC), as well as EP828, a commercially available diglycidyl ether of BPA (EEW 172 g/eq., Japan Epoxy Resin Co. Ltd) were formulated at room temperature with methanol soluble lignin obtained from eucalyptus as a natural curing agent. In order to obtain optimal crosslinking architecture of cured resin plates, the molar ratio of epoxy group to free hydroxyl groups was maintained at the ratio of 1:1. The EEW of the obtained resins is tabulated in Table 1. Only the aromatic hydroxyl groups of lignin were assumed to participate in the curing reaction (Fig. 2). Furthermore, 1-(2-cyanoethyl)-2-ethyl-4-methylimidazole (2E4MZ-CN), a hardening accelerator, was also added in the amount of per hundred ratio (phr, 1/100 g of epoxy resin). The final mixture was dissolved in ~ 30 mL of THF and stirred for 90 min to obtain a homogeneous mixture. Removal of THF was accomplished by transferring onto a polytetrafluoroethylene sheet in a vacuum oven at 60 °C for 1 h. The resins synthesized from FDGTE and standard catechin compound were pressed at 70 °C, and curing was performed at 132 °C for 3 min, 141 °C for 2 h, and finally, 165 °C for 3 h. Different curing temperatures were determined for the resin obtained from HDGTE that was pressed at 70 °C, and

was cured at 110 °C for 1 min, 120 °C for 2 h, and 150 °C for 3 h. The curing temperature was monitored through differential scanning calorimetry (DSC) curve in order to ensure the complete curing.

2.2.9. Swelling ratio and insoluble part determination of the cured resins

Swelling measurements of the networks were conducted with THF as the diffusing solvent. The differences in weight between dried and swollen epoxy networks were used for deducing the swelling percentage. For each measurements, samples (30-50 mg) were immersed in THF (20 mL). After 24 h of immersion, the samples were removed and subjected to brief drying with filter paper, and their weights were measured. The swelling ratio (SRi) was calculated according to the equation 5:

$$SRi = \frac{m1 - m0}{m0} \ldots \ldots \ldots \ldots \ldots (5),$$

where m_0 and m_1 refer to the initial and final weights of the samples prior and subsequent to immersion. The SRi of the material is the average value of duplicate measurements.

Subsequent to the swelling ratio measurement, the samples were dried for 24 h in a vacuum oven at 80 °C. The insoluble fraction (IF) was calculated according to the following equation 6: $IF = \frac{m2}{m0} \ldots \ldots \ldots \ldots \ldots \ldots \ldots (6),$

where m_2 is the sample weight subsequent to drying.

2.2.10. Analysis of the synthesized epoxy resins

^{1}H NMR spectra was obtained using JEOL nuclear magnetic resonance spectrometers (ECX-400 JEOL; USA). The sample (10 mg) was dissolved in of DMSO-d_6 (500 µL), and NMR spectrum was obtained.

The thermal degradation analysis of the synthesized epoxy resins was conducted using a thermogravimetric analyzer (TG/DTA SII EXSTAR 6300, Seiko Instruments Inc., Chiba, Japan) over a temperature range of 40 °C to 800 °C at the heating rate of 5 °C min^{-1}and under nitrogen atmosphere (flow rate of 200 NmL/min). Approximately 5 mg of samples were used, and weight loss temperature curves were recorded.

The mechanical properties of cured epoxy resins was evaluated by measuring flexural strength. The flexural test was conducted using Instron universal test machine (Model 5567), using specimen size of $40 \times 10 \times 3$ mm. The flexural strength of the synthesized specimen was measured using a 3-point bending test with a span length of 50 mm and a crosshead speed of 1.0 mm/min, respectively.

DSC (SII EXSTAR DSC 6100, Seiko Instruments Inc., Chiba, Japan) was used to determine glass transition as well as curing temperatures of the epoxy networks over the temperature range of 40 °C to 300 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

2.3 RESULTS AND DISCUSSIONS

2.3.1. Anlaysis of glycidyl ether of catechin

The epoxidation of commercial as well as green tea extracted catechin was conducted under identical experimental conditions using ECH under alkaline conditions as described in 2.2.6 section. The catechin samples were monitored through ^{1}H NMR prior and subsequent to glycidylation; obvious changes were observed in the ^{1}H NMR spectrum as shown (Figs. 5-7). Hydroxyl signals were clearly observed at 8-10 ppm in the original samples, whilst such signals could not be observed following glycidylation of the same sample, confirming the incorporation of epoxide ring. Furthermore, signals corresponding to methylene and methine proton signals appeared at 2.79-4.39 ppm, with the CH_2-O protons yielding resonance signals at 3.92 and 4.39 ppm, as reported previously (Auof et al., 2013, Benyahya et al., 2014, Nouailhas et al., 2011). However, these signals could not be observed in the NMR spectrum of green tea extracts. Other aromatic proton signals were observed at 6.05-7.25 ppm in all samples (Figs. 5-7). Thus, these NMR data confirmed the successful epoxidation of green tea catechin with ECH.

Furthermore, the ratio of the major reaction products was found to be different for the two types of synthesized resins, GEHDGTE and GEFDGTE. This may be attributed to a decrease in the major catechin compounds during heat drying (Ross et al., 2011), which affect the reaction product. However, the yield of epoxy resin using green tea extract as well as standard catechin, compound was found to be greater than 100%, which is much higher than the corresponding yield from fossil fuel-based BPA

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(70%), as shown (Table 1). The epoxy yield was calculated from equation 7 (Ferdosian et al., 2014):

$$\text{Yield (\%)} = \frac{S}{L\,(1+0.264)} \times 100 \dots\dots\dots\dots\dots\dots \text{(7)},$$

where S, L, and 0.264 represents the weight of dried epoxidized lignin, dried green tea extract in each epoxidation run, and the stoichiometric amount of ECH attached per 1 g of resin, respectively.

2.3.2 Thermal degradation and thermal stability of the synthesized resins

Thermograms of cured films are shown in Fig. 8. Thermograms obtained from thermogravimetric analysis (TGA) clearly indicates good thermal stability of the cured resin up to a temperature of 169 °C with a minimum amount of weight loss, which is possibly due to the minimum amount of unreacted components. The heat-resistant temperature (T_s) is a characteristic of the thermal stability of the cured resins, and is calculated from the temperature difference at 5% and 30% weight loss (T_{d5} and T_{d30}, respectively) obtained from TGA curves. The statistic heat resistant index temperature (T_s) was determined by using equation 8 (Auof et al., 2013a, Auof et al., 2013b, Bibiao et al., 2001, Benyahya et al., 2014):

$$T_s = 0.49[T_{d5} + 0.6 \times (T_{d30} - T_{d5})] \dots\dots\dots\dots\dots\dots 8$$

The decomposition temperatures resulting in 5% and 30% weight loss of the resins cured with lignin i.e., GEC-Lg and GEFDGTE-Lg, were found to be above 300 °C, as detailed in Table 2. The data obtained indicates the good thermal stability of the cured films. However, the decomposition temperature resulting in 5% weight

loss and Ts of lignin-cured resin GEHDGTE-Lg were found to be lower than those of GEFDGTE-Lg. This may be attributed to the degradation or epimerization of the catechin compounds during extended periods of heat drying at 80 °C, which causes the significant decrease in the amount of polyphenol content typically observed following heat treatment (Ross et al., 2011); this, in turn, affects the ratio of the byproducts obtained after synthesis reaction. The low content of free hydroxyl groups in the heat-dried sample also suggests changes in the structure. The major decomposition peak temperatures of GEC-Lg, GEFDGTE-Lg, GEHDGTE-Lg, and glycidyl ether of BPA cured with lignin (GEBPA-Lg), however, were found at similar temperatures (376 °C, 378 °C, 373 °C, and 393 °C, respectively). Marked differences were observed in the thermal stability and initial decomposition temperature of the resins synthesized in this experiment compared to those synthesized using the same substrate (Benyahya et al., 2014). This may be attributed to the use of lignin as a natural curing agent; lignin is usable as a hard segment in epoxy resin network, which increases the glass transition of the resultant polymer network. Therefore, the use of lignin as a curing agent could induce relatively high chain rigidity in the polymer network due to increase crosslinking (Abdul Khalil et al., 2011). The results obtained also suggest that employment of lignin as a natural curing agent is a better option compared to various commercially available curing agents. Thermal decomposition temperatures of 260 °C to 310 °C have been reported by different research groups utilizing different biomasses (Auof et al., 2013a, Auof et al., 2013b, Kuo et al., 2014, Sasaki et al., 2013, Benyahya et al., 2014)

The non-volatile residue at 600 °C and 800 °C were large, amounting to 40% and 35% in the case of GEC-Lg, as opposed to 38% and 33%, respectively, with GEFDGTE-Lg, and 28% and 25%, respectively, with GEBPA-Lg. The lowest char yields amounting to 16% and 9% were observed from GEHDGTE (Table 2).The higher char yield implies that incorporation of lignin moiety into the epoxy matrix elevates the flame retardation of the epoxy resin. Increased char formation potentially limits the production of combustible carbon-containing gases, decreases the exothermicity of pyrolysis reactions, as well as decreases the thermal conductivity of the surface of burning materials (Krevelen, 1975). The biomass content in the synthesized epoxy resin that was calculated based on the yield of resin, and the amount of lignin used for curing, was found to be highest in the case of GEC-Lg (84%), followed by GEFDGTE-Lg (81%) and GEHDGTE-Lg (72%), and lowest in the case of GEBPA (34%; Table 2). The biomass content in the synthesized epoxy resin was calculated using equation 9:

$$\text{Biomass content (\%)} = \frac{S - (S \times 0.264) + Lg}{T} \times 100 \dots\dots\dots\dots\dots\dots (9),$$

where S is the weight of dried epoxidized lignin (g), Lg is the amount of lignin used for curing, T is the total amount of lignin, hardening accelerator, and total cured epoxy resin (g), and 0.264 is the stoichiometric amount of ECH attached per g of resin.

2.3.3 Swelling ratio and insoluble parts

As shown in Table 3, swelling in THF was observed with GEBPA-Lg (5% swelling) but not with GEC-Lg, GEFDGTE-Lg, and GEHDGTE-Lg, indicating the high crosslinking density of catechin based epoxy networks. Swelling ratio provides information about the crosslinking density of resins, while the soluble part provides quantitative information of non-crosslinked networks. The higher crosslinking density is characterized by the short distance between the crosslinking nodes, resulting in lower absorption of the solvent (THF). The presence of two epoxy groups on the same aromatic ring restricts the distance between nodes in the polymer network, thereby increasing the crosslinking density (Benyahya et al., 2014, Nouailhas et al., 2011).

The participation of every epoxy networks of GEC-Lg, GEHDGTE-Lg, and GEFDGTE-Lg could be reinforced by the soluble part values obtained. The soluble part of green-tea based epoxy networks were 1%, which is within the experimental error. On the other hand, the GEBPA-Lg network exhibited highest soluble part amounting to 6%, which also reflects the longer distance between crosslinking nodes leading to increased absorption of solvent (THF). Hence, these bio-based networks are highly crosslinked polymers with three dimensional networks compared to GEPBA-Lg network. Taken together, these results suggest that the general properties of the bio-based epoxy networks synthesized in the present study are comparable with those of the BPA-based polymer networks, and are therefore, potentially good candidate to substitute for BPA-based epoxy polymer.

2.3.4. Glass transition temperature

DSC was employed for the determination of glass transition temperatures at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Glass transition temperature (Tg) is reported as the transition mid-point of the change in heat capacity during the heating cycle. Optimal Tg was obtained through various stoichiometric variation of lignin and epoxy resin. Tg is a valuable characterization parameter associated with an epoxy material, and can provide very useful information for estimating the maximum operating temperature with regard to the enduring performance. The highest Tg values were obtained for GEC-Lg and GEFDGTE-Lg (178 °C and 173 °C, respectively), while those of GEHDGTE-Lg and GEBPA-Lg were observed to be 155 °C and 150 °C, respectively (Table 3). The Tg values obtained for the catechin-based epoxy networks synthesized in this study further valorize them.

2.3.5. Flexural strength

The flexural strengths of GEC-Lg, GEHDGTE-Lg, and GEFDGTE-Lg were found to be 63 MPa, 56 MPa, and 40 MPa, respectively, while that of DGEBA-Lg was found to be lowest of all (29 MPa), as shown. (Table 3). The higher rigidity of the resin could be attributed to the combination of aromatic raw material of low molecular weight and the hard segment of the natural curing agent, lignin, which has average molecular weight. The thermal and mechanical properties so obtained showcase the practical applications of epoxy resins synthesized from green tea extract.

Chapter 3

Conclusions

The present study examines the feasibility of using catechin as an aromatic substrate, for the synthesis of bio-based epoxy resin. All the obtained results suggest that substrate extraction method and purification steps are both an important parameters to be determined in the process of substrate preparation for the synthesis of epoxy resin, which not only effect the substrate quality, but also the thermochemical properties of the synthesized resins. This study serves to advance the field of polymer synthesis by utilizing green tea catechin as the substrate for the synthesis of bio-based polymer, and also suggests that the integration of industrial tea waste management could offer the potential for the development of sustainable biomaterials that will lead to a new manufacturing model. Hence, this study provides the novel insights into the field of polymer chemistry by reporting the successful epoxidation and curing of green tea-based catechin, resulting in improved thermal stability of the synthesized epoxy resin, with potential application in the field of electronics. Moreover, this study completely supports the concept of green chemistry by utilizing water as an extraction solvent, green tea catechin as the substrate, and lignin as a natural curing agent.

Chapter 4

Epoxy resin synthesis using low molecular weight lignin separated from various lignocellulosic materials

4.1. Introduction

Biomass has received considerable attention because of its renewable and environmentally friendly nature. Lignocellulosic materials containing cellulose, hemicellulose, and lignin as their main constituents, are one of the most abundant renewable organic resource present on the earth. The bioconversion of both cellulose and hemicellulose for production of biofuel ethanol is being studied intensively [Priya and Bisaria, 1998; Stephen et al., 2013). However, lignin, which is one of the abundant constituents in the lignocellulosic material, is used only as a fuel or manure. The strong combination of lignin with cellulose and hemicellulose makes it harder to isolate for effective utilization. Hence, the development of a pretreatment method for the efficient separation of lignin and its utilization as a bio-based material is required. A promising pretreatment cab be steam explosion, which has several advantages compared to other alternatives such as reduced capital investment, no adverse environmental impact with greater energy efficiency and no use of hazardous process chemicals.

Epoxy resins with good thermal resistance and superior mechanical properties are the most important thermosetting materials, which are commercially desirable in

modern industries. The use of epoxy resin as coatings, electrical or electronic laminates, adhesives, flooring and paving shows the application versatility of epoxy resin. The most commercially available epoxy resin comes from the synthesis of bisphenol A with epichlorohydrin, which represents 90% of the epoxy precursor in the world. However, bisphenol A is an environmental hormone that mimics human estrogen, and can therefore cause impotency as well as cancer (Keri et al., 2007). This makes bisphenol A undesirable as a raw material for epoxy resin synthesis. The increasing global energy requirement as well as greater environmental awareness also leads to bisphenol A being considered a less desirable material because it is derived from a fossil source.

Hence, there is an urgent need to investigate a bio-based substitute for bisphenol A for the synthesis of epoxy resin. The use of renewable resources as a bio-based raw material for the synthesis of epoxy resin has been applied over the past decades. Recent advances in the synthesis, properties and applications of thermosetting materials derived from renewable resources have been shown by various studies. Vegetable oils have been used as a substrate for epoxy resin synthesis. Wang and Schuman, 2013; Wang et al., 2013 have shown the importance of soybean oil as a substrate for bio-based epoxy resin. Similarly, chlorinated soy-oil based epoxy resin has also been utilized for the same purpose (Thulasiraman et al., 2009). Itaconic acid (Ma et al., 2013), biomass-based furfural (Zhao et al., 2015), and organic solvents soluble extractives from green tea (Basnet et al., 2015) have been used as bio-based raw materials to synthesize epoxy resins. The bio-based

epoxy resins have shown interesting thermal and mechanical properties, comparable with those synthesized from bisphenol A. Hence, lignocellulosic biomass can be an excel-lent substitute for bisphenol A as a raw material of epoxy resin.

To develop cured and high bio-based-content epoxy resin, we studied two processes. First, the glycidylation of a low molecular weight lignin extracted from steam-exploded lignocellulosic biomasses(softwood, hardwood, and herbaceous plant), using tetramethylammonium chloride (TMAC) as a water-soluble phase transfer catalyst, which makes the epoxy resin synthesis easier than other water-insoluble catalysts such as tetrabutylammonium bromide (TBAB). Second, we performed the curing of synthesized epoxy polymer network with bio-based curing agent i.e., the lignin itself. The chemical and thermal properties of the synthesized epoxy resins were compared with a commercial epoxy polymer network synthesized from bisphenol A. This study is important since these natural biomass extracts open a route to a new renewable resource usable for polymer synthesis.

4.2. MATERIALS AND METHODS

4.2.1. Samples

Cedar (*Cryptomeria japonica*), eucalyptus (*Eucalyptus globulus*), and bamboo (*Phyllostachys pubescens*) were chopped into woodchips (2–4 cm in length and 1–3 cm in width) and used as plant biomass samples.

4.2.2. Steam explosion.

Sample pretreatment, which is one of the most important steps for the detachment of lignin from lignocellulosic biomass, was conducted with the steam explosion apparatus equipped with a reactor of 2 L capacity (steam explosion apparatus NK-2L; Japan Chemical Engineering and Machinery Co. Ltd, Osaka, Japan) (Asada et al., 2012; Sasaki et al., 2012). Two hundred grams of sample per batch was introduced into the reactor and exposed to the saturated steam of 3.5 MPa (243 °C) and steaming time of 5 min. In this apparatus, the prescribed temperature was reached within a few seconds. After exposure to the saturated steam, a ball valve at the bottom of the reactor was opened suddenly to bring the reactor rapidly to atmospheric pressure. The product containing liquid–solid materials was obtained as the steam-exploded product in the receiver.

4.2.3. Extraction and component analysis.

The amounts of the components (i.e., water-soluble material, methanol-soluble lignin, holocellulose (cellulose and hemicellulose), and sulfuric acid-insoluble residue) in the steam-exploded product were measured by the extraction and separation procedure as shown in Fig. 9. Five grams of each sample (in triplicate) was extracted with 300 mL of distilled water (DW) for 24 h at room temperature with stirring. The solid and liquid materials were separated by filtration, and the filtrate (i.e., water-soluble material) was recovered from the liquid, and then concentrated, dried, and weighed. The precipitate was extracted with 150 mL of methanol at room

temperature for 24 h with stirring to dissolve the methanol-soluble lignin (a low molecular weight lignin).

After concentration and drying off the extract, the methanol-soluble lignin was weighed. The residue from the methanol extraction consisted of holocellulose, Klason lignin (a high molecular weight lignin), acid-soluble lignin, and others. One gram of this residue was added with 15 mL of 72% (w/w) sulfuric acid and kept at room temperature for 4 h. After 4 h, the mixture was transferred to a 100 mL conical flask, then washed with 560 mL DW, and then autoclaved for 1 h at 121 °C. After the sulfuric acid-insoluble residue was washed with 1 L DW, it was oven dried at 105 °C to a constant weight. The amount of holocellulose was calculated by subtracting the amount of sulfuric acid-insoluble residue from the amount of methanol-soluble residue. All analytical determinations were performed in triplicate and the average values are shown.

4.2.4. Synthesis of epoxy resin from methanol-soluble lignin.

A 1000 mL four-necked flask equipped with a condenser, septum cap and a stirrer was charged with 0.1 mol of methanol soluble lignin dissolved in 50 mol of epichlorohydrin (For e.g. 10 g lignin in about 400 mL of epichlorohydrin). The gram equivalent weight, which is defined as the mass of a given substance which contains one part by weight of replaceable hydroxyl groups, were found 115, 115, and 118 g/eq, belonging to cedar, eucalyptus and bamboo lignin, respectively (determined by the acetic anhydride and pyridine method; Hitachi Chemical Techno Service Co.,

Ltd.). Hence, the obtained hydroxyl equivalent weight of the lignin refers to the mass of hydroxyl groups that could be replaced during reaction with epichlorohydrin.

The solution of TMAC (0.25 g in 9.25 mL DW) was added dropwise after 10 min of the reaction. The suspension was heated at 70 °C under nitrogen (N_2) flow with continuous stirring at 250 rpm for 8 h until the completion of the reaction. The water-soluble TMAC catalyzes the reaction resulting the opening of the epoxy ring and detaching the hydrogen chloride. Next, the epoxy ring was reconstructed with addition of sodium hydroxide. The resulting mixture was then cooled to 45 °C, followed by the addition of concentrated sodium hydroxide (50 wt%, 4.8 g in 4.8 mL DW) and maintained under N_2 flow until completion, with stirring for another 3 h. The organic layer was then separated and washed three times with DW (100 mL each time) to remove NaCl (by product of reaction) and the remaining catalyst. Finally, the excess epichlorohydrin and organic solvent was distilled off under reduced pressure at 70 °C to obtain the epoxidized resins from different biomasses i.e., cedar, eucalyptus, and bamboo.

The obtained lignin epoxy resins were further dissolved in methyl ethyl ketone (MEK) as a solvent. MEK was used as a solvent during ring closure reaction because it can dissolve lignin epoxy resin whilst insoluble in water. This property of MEK is favorable to wash out NaCl produced as a byproduct during ring closure reaction leaving final epoxidized product in the organic portion. The volume of MEK was fixed at 20 times the amount of epoxy resin, e.g., 18.1 g of epoxy resin in 362 g MEK. The ring closure reaction of the synthesized resins was conducted in a four-necked 1000 mL flask, which was charged with epoxidized lignin obtained from different

biomasses followed by the addition of aqueous NaOH (30 wt%, 0.39 g in 0.93 mL DW) at 70 °C under N_2 flow with continuous stirring at 250 rpm for 1 h. After that the temperature was cooled down and the reaction mixture was washed with DW (100 mL, three times) and the organic solvents (MEK and remaining epichlorohydrin) were distilled off under reduced pressure using an oil bath at 120 °C.

The final product was then dried in a vacuum oven at 40 °C overnight and weighed to obtain 9.4, 10.9, and 12.2 g of final epoxidized resin from cedar, eucalyptus, and bamboo with epoxy equivalent weights of 337.5, 342.5, and 345.4 g/eq, respectively. The epoxy equivalent was determined by titration of the product dis-solved in HCl/dioxane solution with a solution of NaOH in methanol (Sasaki et al., 2011). All the chemicals used in this experiment were supplied by Wako Pure Chemical Industries Ltd., Japan and were used without further purification.

4.2.5. Synthesis of cured epoxy resin

The cured networks of lignin epoxy resins and a commercial epoxy resin EP828 (diglycidyl ether of bisphenol A; Japan Epoxy Resins Co. Ltd.) were prepared with lignin as a bio-based curing agent and TD2131 (a phenol novolac; DIC Corp.) as a chemical curing agent, in 1:1 molar ratio of epoxy group to hydroxyl equivalent groups, to obtain the optimal cross-linking of cured epoxy samples. Furthermore, 1-(2-cyanoethyl)-2-ethyl-4-methylimidazole (2E4MZ-CN), a hardening accelerator, was also added in the amount of per hundred ratio (phr). The mixture was dissolved in tetrahydrofuran (THF, about 30 mL) then stirred for 15 min at room temperature.

The solution mixture was then transferred into a sheet of PTFE to remove THF in a vacuum oven at 50 °C for 1 h. The curing process of epoxy resin was performed at 110 °C for 0.1 h, 150 °C for 2 h, and then 180 °C for 3 h, as determined from the DSC curve.

4.2.6. Analyses

A nuclear magnetic resonance (NMR) spectrometer (ECX-400; JEOL, USA) was used to obtain ^{1}H NMR spectra. Each 5 mg sample was dissolved in 500 μL of DMSO-d_6 and was measured by NMR spectroscopy. The FTIR spectral analysis of cedar, eucalyptus, and bamboo lignin, and their respective epoxy resins, was performed on an FTIR spectrophotometer (FTIR 420; JASCO Co.,) using KBr pellets containing 1% finely ground samples. Each spectrum was recorded using 32 scans ranging from 4000 to 500 cm^{-1}, with a resolution of 4 cm^{-1} in the transmission mode. The purity of methanol-soluble lignin was measured by removing impurities with 72% (w/w) sulfuric acid. The thermogravimetric (TG) curve was measured using a TG analyzer (TG/DTA SII EXSTAR 6300; Seiko Instruments Inc., Chiba, Japan) under an atmosphere of nitrogen (heating rate of 5 °C/min) using alumina as a primary standard. The thermal tests were performed in triplicate and average values are shown.

4.3. RESULTS AND DISCUSSIONS

4.3.1. Extraction and separation process of steam-exploded plant biomasses

The extraction and separation of steam-exploded samples were performed in two processes as shown in Fig. 10. The pretreated cedar at a steam pressure of 3.5 MPa (243 °C) and a steaming time of 5 min was extracted with DW and methanol as extracting solvents. In the case of Process 1, 100 g (dry weight basis) of steam-exploded cedar was extracted with 6 L of DW at room temperature with stirring, and separated into two fractions: water-soluble material (9.2 g) and water-insoluble residue (90.8 g). Because the water soluble material contains not only oligosaccharides and monosaccharides derived from hemicellulose but also water-soluble polyphenols derived from lignin, they are expected to be used as functional food compound (Asada et al., 2012). The water-insoluble residue was extracted with methanol at 80 °C using a Soxhlet apparatus, which yielded 19.4 g of methanol-soluble lignin with a weight-average molecular weight of 1600. This methanol-soluble lignin can be used as a raw material for epoxy resin synthesis (Nakamura et al., 2001). Furthermore, the methanol insoluble residue was hydrolyzed enzymatically into glucose (21.9 g), which can be a substrate for the production of alcohol, lactic acid, and others (Asada et al., 2011). The water-insoluble residue in the case of Process 2, was extracted with methanol at room temperature, giving 13.6 g of methanol-soluble lignin with a weight-average molecular weight of 1330, whereas the methanol-insoluble residue was hydrolyzed enzymatically into glucose (27.5 g). The decrease in the amount of methanol-soluble lignin during Process 2 was described as a low solubility of high-molecular weight lignin at low temperature. This led to the extraction of low-molecular weight lignin at low temperature. Likewise, the amount of glucose obtained through Process 2 was higher than that

from Process 1. The decrease of the glucose in Process 1 occurred because of the change in the cellulose structure at high-extraction temperature (80 °C), which in turn, led to this material becoming resistant to enzymatic saccharification. Any scientific process that leads to various favorable results is more desirable to adopt as a working protocol. Hence, Process 2 was selected for conducting further experiments because this process leads to the extraction of low molecular weight lignin that is easier for resinification at room temperature, reducing the energy consumption. Another benefit of this process is the production of glucose through enzyme hydrolysis, which is one of the important precursors in biofuel industry for the production of bioethanol. Therefore, the methanol-soluble lignin extracted through Process 2 was used as a raw material for resinification. The solubility of commercial lignins, as well as the lignin extracted from the steam-exploded cedar, were checked for their solubility in different organic solvents such as THF, methanol, epichlorohydrin, and water (Table 4). These results show that the commercial lignins are slightly or not soluble in organic solvents but soluble in water. The solubility of lignin in the organic solvent is an important parameter in the field of electronic circuit boards because the electric appliances are generally derived from organic soluble lignin. In case of the lignin that is not soluble inorganic solvent, it must be modified in order to make it soluble in desired organic solvent for its application in resinification process (Jianglei et al., 2014). Hence, methanol soluble lignin extracted in this work is more desirable as a raw material than any other commercial lignins, and makes it more applicable in the field of electronics.

4.3.2. Extraction of methanol soluble lignin from various steam-exploded plant biomass

The total components extracted from steam-exploded biomass (i.e., cedar, eucalyptus, and bamboo) at the steam pressure of 3.5 MPa and steaming time of 5 min is shown in Fig. 11. The weight ratios of the extracted components were expressed on the dry weight basis of steam-exploded plant biomass. Regardless of the biomass type, the ratio of water-soluble material from different biomass, which includes monosaccharide, oligosaccharide, 5-HMF, furfural, and organic acids, were observed to be similar i.e., about 9%. The chemical and structural compositions of biomass vary with the geographical locations and plant species. A similar effect could also be observed in this study. The ratios of methanol-soluble lignin extracted from steam-exploded varied greatly, with 13.6%, 23.6%, and 27.2% from cedar, eucalyptus, and bamboo, respectively. Three different phenyl propane units, or monolignols, or lignin precursors (i.e., p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol) are responsible for lignin biosynthesis. These precursors vary only in their degree of methoxylation. These lignols are incorporated into lignin in the form of the phenyl propanoids such as guaiacyl, syringyl, and p-hydroxyphenyl moieties. Softwood biomass such as cedar is composed of guaiacyl lignin, which consists almost entirely of guaiacyl moieties with small quantities of syringyl moieties. This is the reason why softwood biomass contains a comparatively large amount of condensed-type lignin, whereas hardwood biomass such as eucalyptus is composed of lignin, which contains not only guaiacyl moieties but also syringyl

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moieties. On the other hand, the herbaceous biomass such as bamboo contains lignin that consists of a mixture of all three moieties (Boerjan et al., 2003). Furthermore, the lignin consisting of guaiacyl moieties (i.e., condensed-type lignin) is difficult to degrade and its degraded product is easy to condense (Ehara et al., 2002). Because the hardwood and herbaceous biomass contain lower amounts of condensed-type lignin than softwood biomass, which is resistant to hydrolysis, this results in increased amounts of extracted lignin in eucalyptus and bamboo than that in cedar. The ratios of holocellulose (i.e., cellulose and hemicellulose), which is a substrate of bioethanol production, extracted from steam-exploded cedar, eucalyptus, and bamboo, were 43.2%, 50.7%, and 46.1%, respectively. Sulfuric acid-insoluble residue, (i.e., high molecular weight lignin) re-condensation products of degraded holocellulose and lignin, and ash, also varied significantly with the type of biomass (Chua and Wayman, 1979; Asada et al., 2005). Hence, the amount of methanol-soluble lignin obtained in the order of bamboo, eucalyptus, and cedar, were in accordance with the references (Boerjan et al., 2003; Ehara et al., 2002). The characteristics of methanol-soluble lignin from various steam-exploded plant biomass is shown in Table 5. The purity of all methanol-soluble lignin was above 99%, which implies that high-purity lignin was obtained in this study. Although the weight-average molecular weights varied significantly with the kind of biomass, the hydroxyl equivalents were almost constant, i.e., 115–118. The hydroxyl equivalent shows the content of free hydroxyl groups that can be epoxidized in a chemical substance. It was found that the methanol-soluble lignin has a low-molecular weight lignin (i.e., 1330–1600) with a comparatively large number of hydroxyl groups (i.e.,

12–14). Furthermore, the molecular weights of the lignins were in the order of bamboo, eucalyptus, and cedar, respectively. The difference in their molecular weights was attributed to the variation of lignin structure of plant biomass as described previously.

4.3.3. Analysis of epoxy resin synthesized from methanol soluble lignin

The epoxidation of methanol-soluble lignin was conducted with epichlorohydrin as described in the experimental section. The ^{1}H NMR and FTIR spectra of methanol-soluble lignin and epoxidized lignin from eucalyptus are shown in Figs. 12 and 13, respectively. The ^{1}H NMR spectrum of epoxidized and non-epoxidized lignin clearly varied. The alkyl and methoxy signals in the non-epoxidized lignin were observed at 1–4 and 3.8 ppm, respectively. However, in the case of epoxidized lignin, the signals belonging to epoxide rings were observed at 2.6–3.0 ppm, confirming the incorporation of epoxy group into the lignin. Furthermore, the weak absorption peak of O–H stretching at 3400 cm^{-1} and the appearance of a new absorption peak at 911 cm^{-1} in the FTIR spectrum corresponded with the epoxide ring, also supports the incorporation of epoxide ring. Similar results were also observed in the cedar- and bamboo-derived samples (data not shown).The epoxy resin yield as well as the epoxy equivalent of biomass-derived resins and bisphenol A-derived resin are shown in Table 6. The amount of epoxy resin yield, regardless of sample types, were similar, i.e., 63.4–70%. This result implies that the biomass-based resin as well as bisphenol A-based resin could be synthesized using the same synthetic route; hence, suggesting that the biomass-derived lignin could be

a good substitute for bisphenol A. The epoxy equivalent value of epoxidized lignin was almost twice as much of epoxidized bisphenol A. The higher epoxy equivalent value of the biomass-derived resins could be explained by the higher molecular weight of the biomass-based lignin over bisphenol A (MW 228), as already mentioned in Table 5. Among the three biomass species, the lowest molecular weight as well as the epoxy equivalent was observed for cedar. This suggests that the epoxidized lignin from this plant species has a large number of functional groups required for curing compared to that of eucalyptus and bamboo.

4.3.4. Thermal properties of various epoxy resins cross-linked with phenol novolac and lignin

Epoxidized lignin was cross-linked with two kinds of curing agents: a bio-based curing agent (i.e., methanol-soluble lignin) and a petroleum-derived phenol novolac (TD2131). The thermal properties (i.e., thermal stability and thermal decomposition) of cured resins were investigated by using TG analysis. Fig. 14 shows the TG/DTA profiles of various cured epoxy resins under a nitrogen atmosphere. In this experiment, the epoxidized lignin derived from eucalyptus and Epikote 828 (EP828), a commercial fossil resource-derived resin, were used for the comparative study. Like-wise, the eucalyptus-derived lignin and Phenolite TD2131, a fossil resource-derived phenol novolac, were used as curing agents. The detailed analysis of TG curves showed that the weight loss of cured epoxy resin increased with an increase in temperature, and at 400 °C, the weight loss increased in the order of epoxidized lignin + lignin, epoxidized lignin + TD2131, EP828 + lignin, and

EP828 + TD2131 (control), respectively. This order followed the amount of lignin content in the cured epoxy resins, i.e., the higher the lignin content, the faster the degradation rate. Similar results could be observed in the cured epoxy resins synthesized from eucalyptus and bamboo lignins (data not shown). The thermal decomposition behavior of the cured lignin epoxy resins could be attributed to the two-step decomposition behavior of lignin itself, which consisted of two stages between 100 °C and 300 °C and between 300 °C and 500 °C. Shen et al., 2010 investigated the thermal decomposition of kraft lignin by TG analysis and FTIR and reported that the detachment of phenolic compounds having an alkyl chain (i.e., phenyl propane units at about 270 °C) and the release of methanol and carbon dioxide caused by the thermolysis of methoxy group binding to the aromatic ring, and the terminal binding of hydroxyl group to the carbon of the side chain, occurred at approximately 380 °C. Therefore, the thermal decomposition of cured epoxidized lignin occurred at a lower temperature than that of the fossil resource-derived epoxy resin, which can be attributed to the aforementioned reason, i.e., it was due to high bio-based (lignin) content. The thermal decomposition temperatures of various cured epoxy resins are listed in Table 7. The decomposition temperature at 5% weight loss (Td_5) and 10% weight loss (Td_{10}) decreased in the order of EP828 + TD2131 (control), EP828 + lignin, epoxidized lignin + TD2131, and epoxidized lignin + lignin, respectively. This suggests that the higher lignin content in cured epoxy resin reduced the decomposition temperatures of Td_5 and Td_{10}. Although, Td_5 of cured lignin epoxy resin was lower than that of the fossil resource-derived cured epoxy resin (i.e., EP828 + TD2131) it satisfy the heat-stability property for solder-dip

resistance, which is 250–280 °C, as required in the electronic field (Sasaki et. al., 2013; Asasda et al., 2012). Benhyahya et al., 2014 reported that the decomposition temperature at 30% weight loss of cured bio-based epoxy resin using a green tea extract (i.e., catechin with isophorone diamine) was 299 °C. This value seems to be much lower than that of the cured lignin epoxy resins because their decomposition temperatures at 10% weight loss were 298–336 °C as shown in Table 7. Therefore, the low molecular weight lignin obtained in this study is a more suitable biopolymer than catechin for the synthesis of heat-resistant bio-based epoxy resins. Among all of the biomass-derived lignin, the thermal decomposition temperatures, Td_5 and Td_{10} of cedar-derived epoxy resin were higher than those derived from eucalyptus and bamboo. This decomposition behavior of cedar-derived resin can be attributed to the lower molecular weight as well as the lower epoxy equivalent weight of cedar lignin, resulting in high thermal stability. Furthermore, the amount of residues (i.e., char yields), which is also an index of incombustibility, were higher than that of the control at decomposition temperatures of 600 °C and 800 °C. This implies that the char formation occurred by a condensation reaction that was caused during the thermolysis process of the lignin (Nakamura et al., 2007). Because the cured lignin epoxy resin has high bio-based content (i.e., more than 80% of lignin), it can be considered as a renewable resource for epoxy resin synthesis. The chemical reagent epichlorohydrin, without which epoxidation cannot be imagined, can also be derived from plant biomass (Dibenedetto et al., 2011). Therefore, in the future there is a possibility that the thermosetting resins could be synthesized using entirely biomass-derived materials.

Chapter 5

Conclusions

A complete study on the utilization of biomass-derived components was conducted. The high-purity (above 99%) low molecular weight methanol-soluble lignins were extracted from the steam-exploded lignocellulosic samples (cedar, eucalyptus, and bamboo). The methanol-soluble lignins were used as a raw material for the synthesis of bio-based epoxy resins, in epichlorohydrin and TMAC under alkaline conditions, whereas insoluble residues were enzymatically hydrolyzed to produce glucose. Good yields of biomass-derived epoxy resins (63.4–68.2%) were obtained, which were in accordance with the yield from bisphenol A (70%), suggesting that the biomass-based as well as the bisphenol A-based resins could be synthesized using the same synthetic route. The resulting polymer networks were cured with biomass-derived lignin as a natural curing agent, or TD2131 as a chemical curing agent. The thermal decomposition temperatures (Td_5 and Td_{10}) of cured biomass-derived components were found to be lower than those of EP828 resin. However, the cured lignin epoxy resins satisfy the heat-stability property for solder-dip resistance. Hence, these high bio-based content resins (more than 80% lignin content) derived from different lignocellulosic materials may be desirable candidates in the field of electronics and also could be an excellent substitute for fossil resource-derived bisphenol A. This study opens the possibility of using these kinds of natural biomass components as a renewable resource for polymer synthesis.

Summary

In recent years public concern about climate change due to excessive fossil fuel consumption has raised tremendously. Different research works are being performed to decrease the release of greenhouse gas like CO_2, or their take up, to reduce the environmental impact. The field of epoxy resin synthesis directly deals with the consumption of fossil resource based BPA, which is prepared by the reaction of two equivalents of phenol with one equivalent of acetone. Structurally, BPA has two phenolic hydroxyl groups which serve as a building block to form several important polymers and polymer additives. Hence, BPA has become an integral part in the field of chemical synthesis. However, in recent years public concern about BPA migration into canned food has increased. The presence of BPA in foods or drinks from epoxy resins, phenol resins, polycarbonates, polyacrylates, polyesters, and lacquer coatings cans can adversely effect on human health and environment as canned foods are sterilized during production at high temperature, rendering the high change of BPA migration from the can coating. The warning issued by The European Commission's Scientific Committee on Food about the tolerable daily intake specification for BPA cannot not be ignored, which mentions that the daily intake of BPA should be lowered to 0.01 mg kg^{-1}. Many studies have ascertained BPA as an endocrine disruptor, which can mimic the human estrogen, resulting the decreased sperm production efficiency as well as lowered sperm count, leading to the infertility in men. Hence, the exposure to BPA during handling possesses high health risks.

The overall aim of this research was to develop different biomass based epoxy resin system and to explore their possibilities to be utilized as a renewable resources, especially in the field of resin synthesis. The environmental concerns related to the fossil rising consumption and hike in the price of petroleum every year, have drawn the interest in alternative renewable resources. The use of biomass as raw material is considered to be the most suitable and renewable primary energy resource for production of alternative bio-fuels and bio-materials. The biorefinery is an emerging field that has a goal to compete with petroleum-based industries. This work was executed through main four steps including; (1) the extraction (in case of green tea) or steam explosion (in case of woody biomass) to open up the biomass structure and break down the lignocellulosic bonding in order to promote separation of lignin from cellulose and hemicellulose, (2) synthesis of epoxidized bio-based resin from the organic solvent soluble extract or methanol soluble lignin from pretreated woody biomass, (3) formulation of the synthesized resins with the natural curing agent i.e. lignin itself, and (4) evaluation of thermogravimetric and mechanical properties of synthesized bio-based resins and comparison with bisphenol A based epoxy resin system.

The performed experiments proved that it is possible to obtain epoxy resin using different biomasses. All resins prepared were fully characterized. All the synthesized resins fulfilled the dip-soldering temperature that required in circuit board industry with good thermal and mechanical property compared to the conventional BPA resin network. Furthermore, the results show that steam exploded methanol soluble lignin has potential to be used as a natural curing agent. This is the

environmentally friendly synthetic route and resin formulation approach, as the substrate as well as curing agents described in this work are biomass-based and show potential applicative interest.

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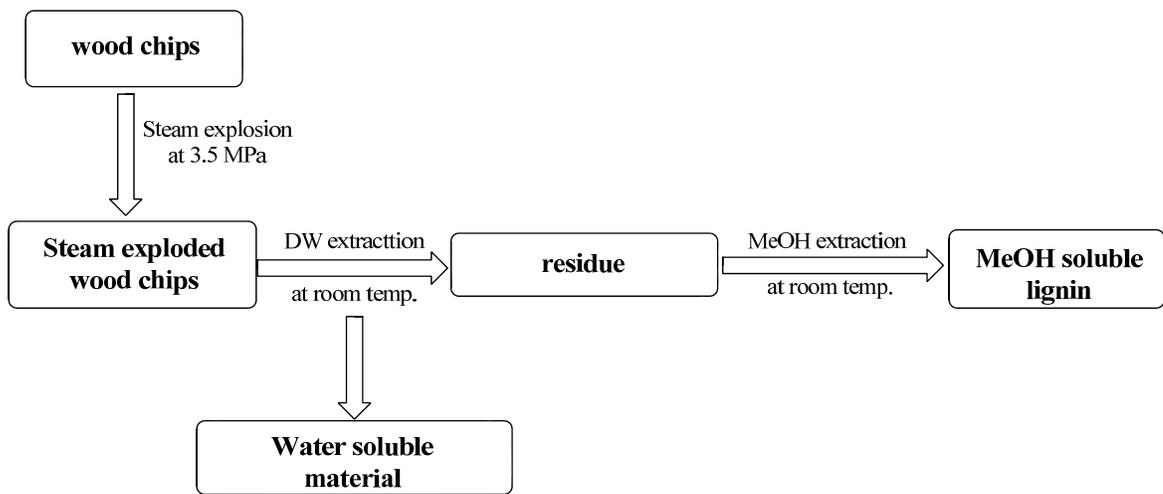
Figure 1: Extraction of lignin
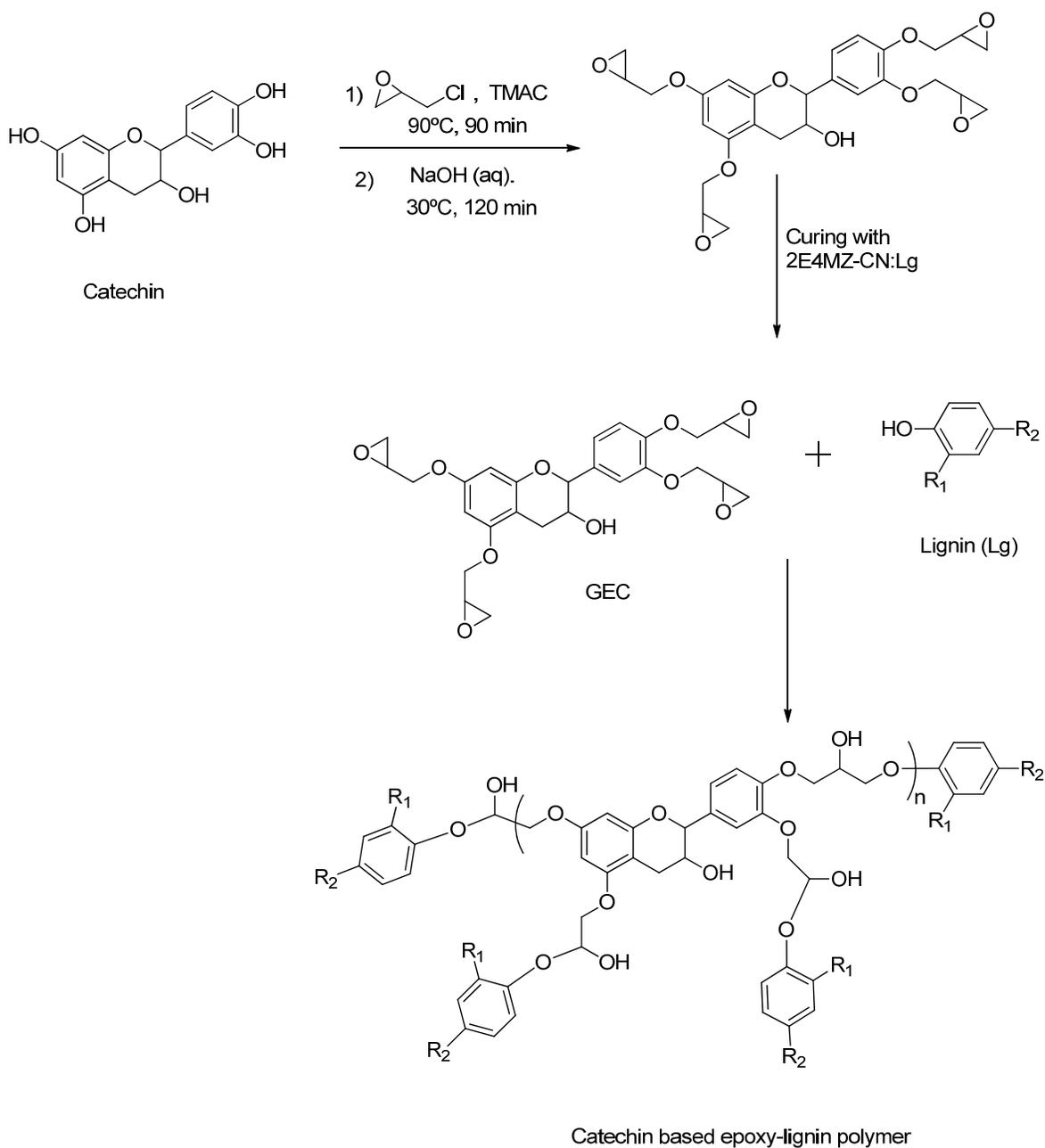
Figure 2: The idealized scheme of catechin epoxidation and networks formation during curing reaction of catechin epoxy-lignin system (where, R_1 represents –OCH3, and R_2 represents –CH=CH-CHO).
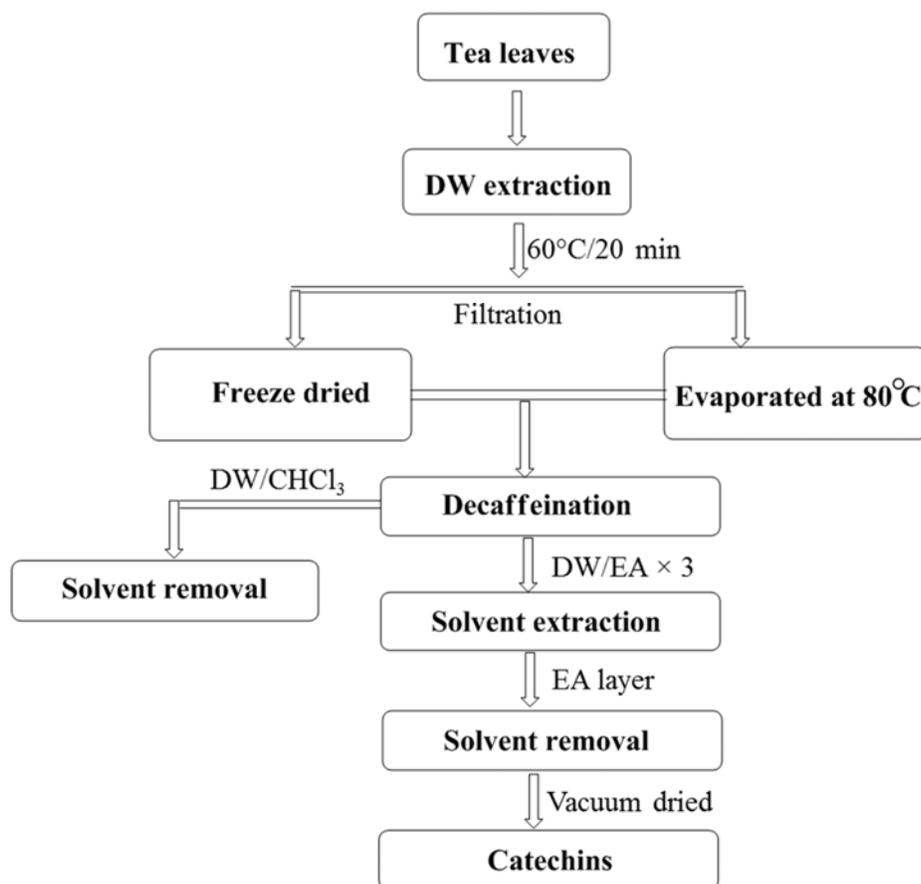
Figure 3: Schematic diagram of tea polyphenol extraction and decaffeination
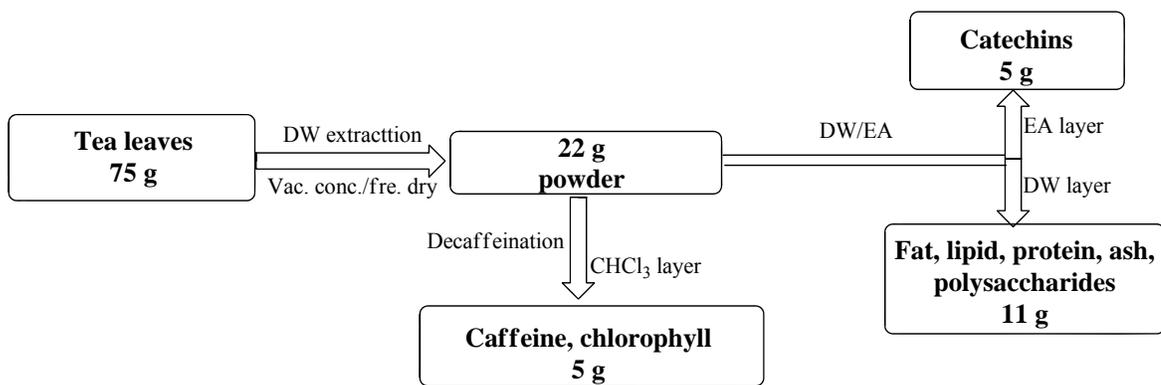
Figure 4: Mass balance of green tea extract.
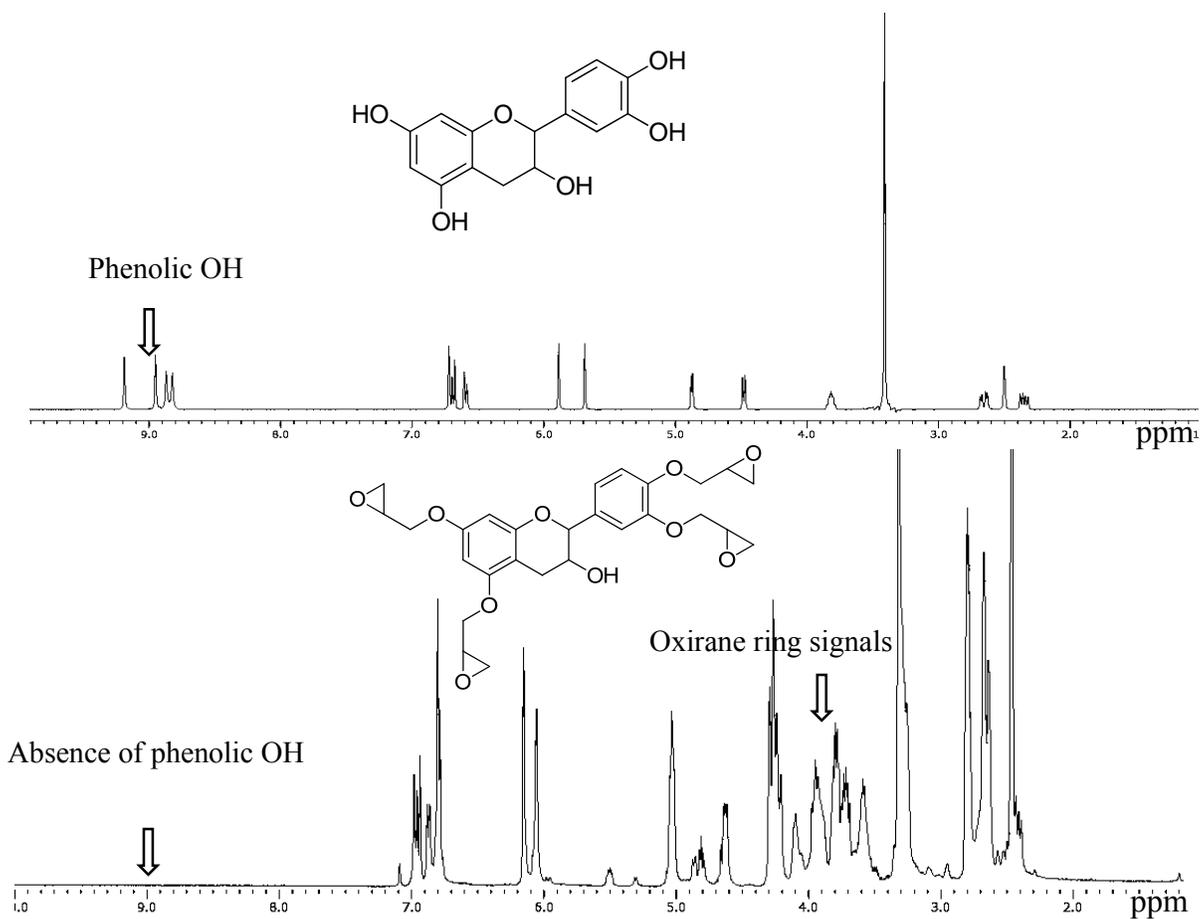
Figure 5: The ^{1}H NMR of catechin and GEC
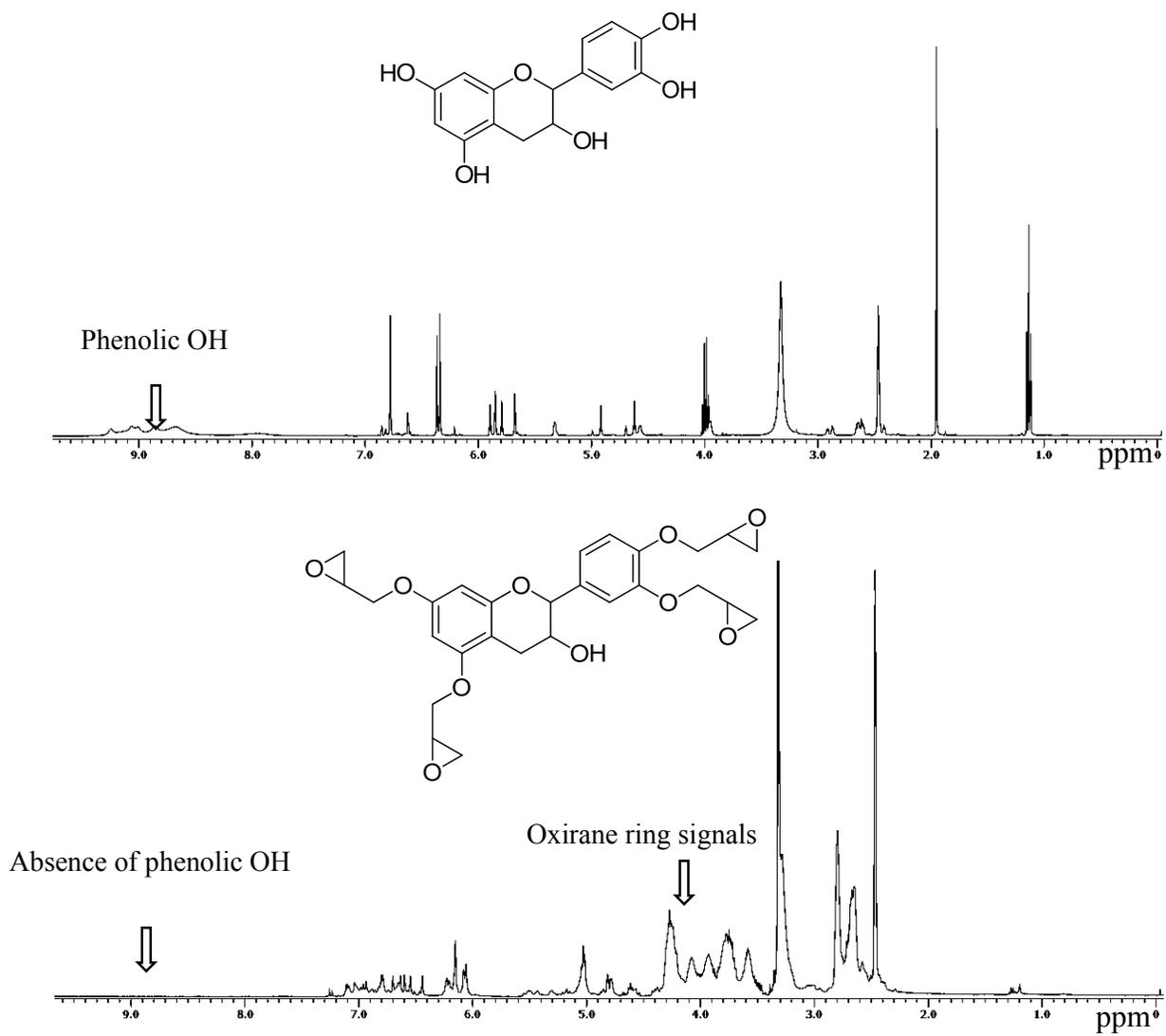
Figure 6: The ^{1}H NMR of FDGTE and GEFDGTE.
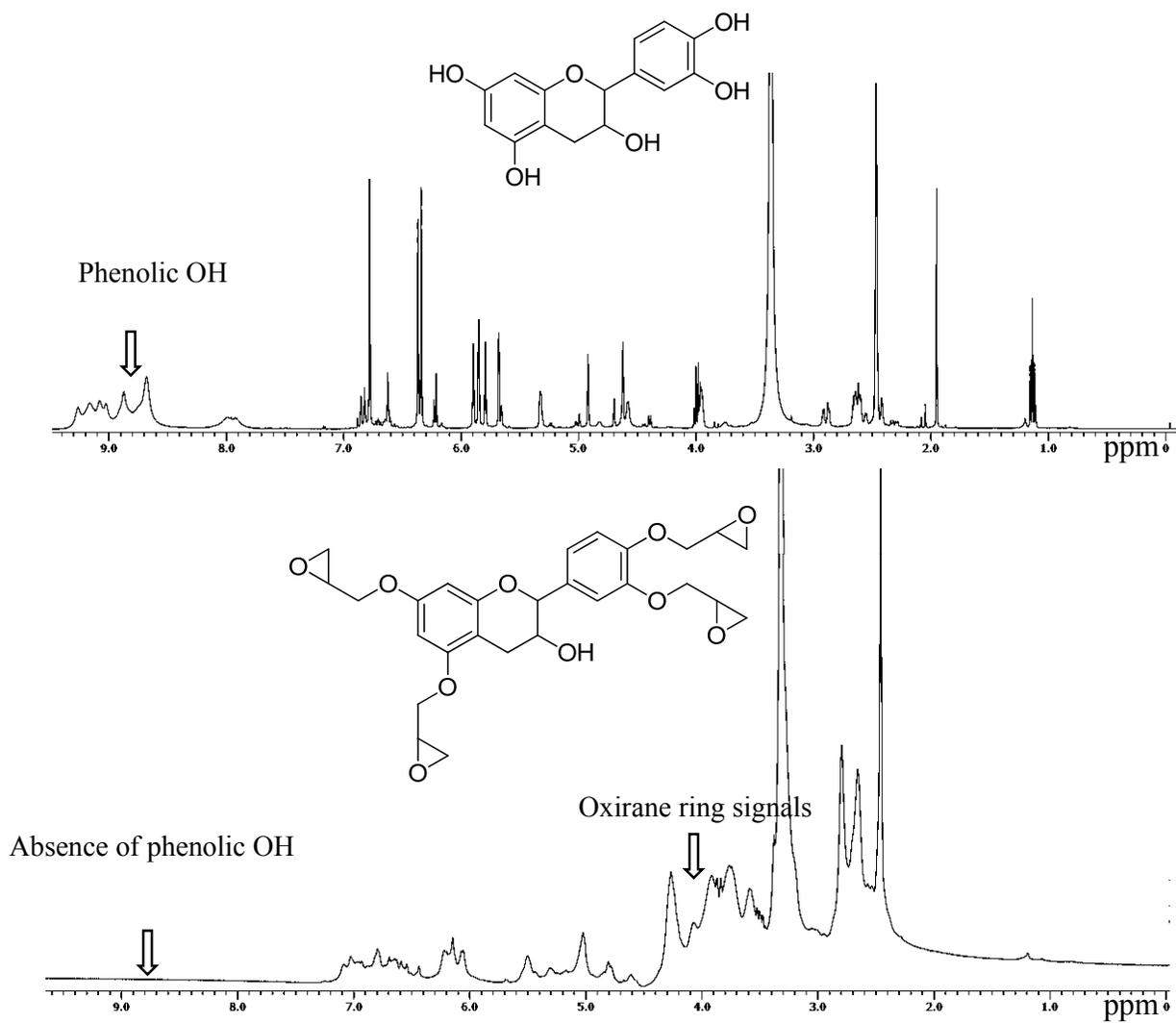
Figure 7: The ^{1}H NMR of HDGTE and GEHDGTE.
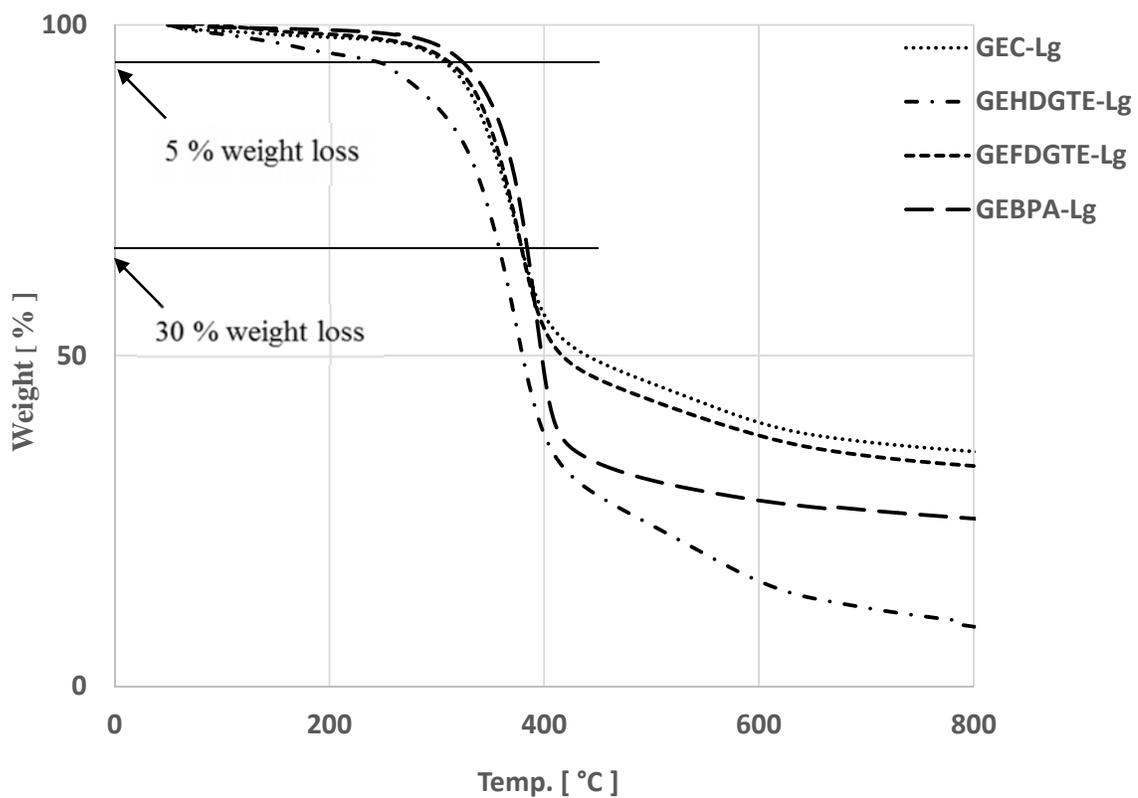
Figure 8: Thermogravimetric analysis traces of GEC-Lg, GEHDGTE-Lg, GEFDGTE-Lg, and GEBPA-Lg cured epoxy resins under nitrogen atmosphere.

Table 1. Hydroxyl equivalent, epoxy equivalent weight, and epoxy resin yield of green tea-based catechin.

Sample	Hydroxyl equivalent g/eq.	Epoxy equivalent g/eq.	Epoxy resin yield (%)[a]
Catechin	54	240(GEC)	106
HDGTE	106	293(GEHDGTE)	92
FDGTE	61	231(GEFDGTE)	108
BPA	114	172(GEBPA)	70

[a] Epoxy resin yield from bio-based substrate calculated by equation 7.

Table 2. Parameters related to thermal stability, decomposition temperatures, char

yields, and biomass content of cured epoxy resins.

System	T_{d5} (° C)[a]	T_{d30} (° C)[b]	T_s[c]	Char$_{600}$ (%)[d]	Char$_{800}$ (%)[e]	Biomass content (%)[f]
GEC-Lg	302	373	169	40	35	84
GEHDGTE-Lg	229	352	148	16	9	72
GEFDGTE-Lg	300	374	168	38	33	81
GEBPA-Lg	320	380	169	28	25	34

[a] Temperature of 5% weight loss under N_2 as given by TGA

[b] Temperature of 30% weight loss under N_2 as given by TGA.

[c] Statistic heat-resistant index temperature calculated by eq. 8.

[d] Char yield at 600 °C under N_2 as given by TGA.

[e] Char yield at 800 °C under N_2 as given by TGA.

[f] Biomass content in epoxy resin calculated by equation 9.

Table 3. Glass transition temperature, flexural strength, swelling ratio and soluble parts of synthesized epoxy networks

System	Glass transition (Tg) (° C)	Flexural strength (MPa)	Swelling ratio (%)[a]	Soluble part (%)[b]
GEC -Lg	178	63	0	0
GEHDGTE-Lg	155	56	0	1
GEFDGTE-Lg	173	40	0	1
GEBPA-Lg	150	29	5	6

[a] Swelling ratio of epoxy networks calculated by equation 5.

[b] Insoluble fraction of epoxy networks calculated by equation 6.
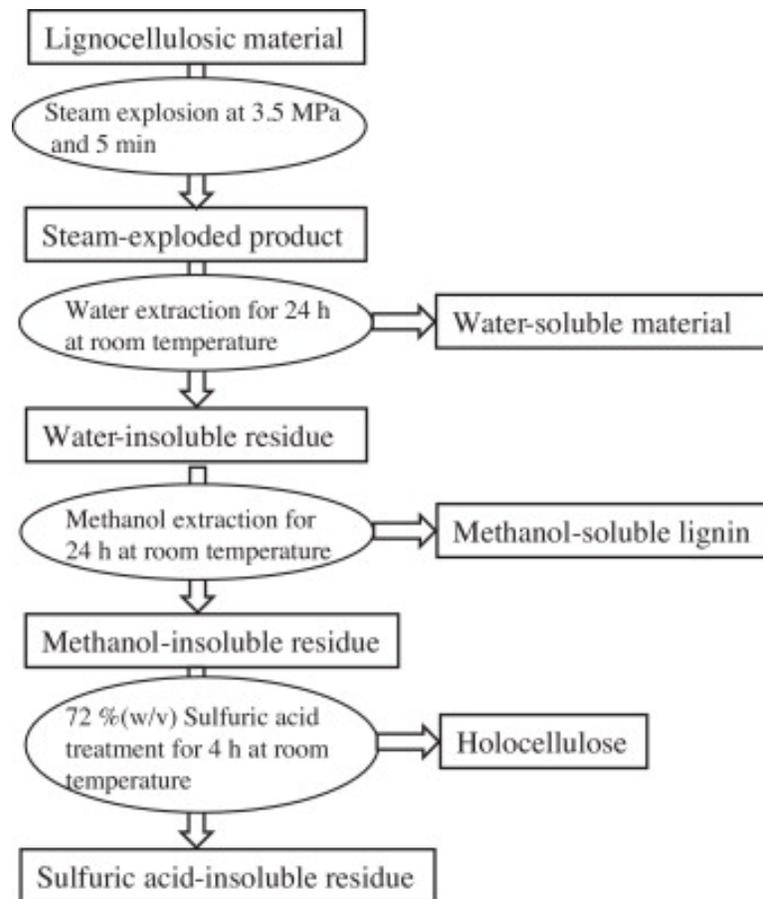
Figure 9: Extraction and separation procedure of lignocellulosic material.

Process 1

```
                Water extraction at        Methanol extraction
                room temperature           at 80°C using           Enzymatic
                                           Soxhlet extractor        saccharification
Steam-exploded ──────────────→ Residue ──────────────→ Residue ──────────────→ Residue
cedar (100 g)        │                         │                        │
                     ↓                         ↓                        ↓
              Water-soluble            Methanol-soluble          Glucose (21.9 g)
              material (9.2 g)         lignin (19.4 g,
                                       Mw 1,600)
```

Process 2

```
                Water extraction at        Methanol extraction
                room temperature           at room temperature     Enzymatic
                                                                    saccharification
Steam-exploded ──────────────→ Residue ──────────────→ Residue ──────────────→ Residue
cedar (100 g)        │                         │                        │
                     ↓                         ↓                        ↓
              Water-soluble            Methanol-soluble          Glucose (27.5 g)
              material (9.2 g)         lignin (13.6 g,
                     ┊                 Mw 1,330)                        ┊
                     ┊                         ┊                        ┊
              ┌─────────────┐          ┌─────────────┐        ┌──────────────────────────┐
              ┊ Functional food ┊      ┊ Epoxy resin ┊        ┊ Alcohol, Lactic acid, etc. ┊
              ┊ compound        ┊      └─────────────┘        └──────────────────────────┘
              └─────────────┘
```

Figure 10: Conversion process of steam-exploded raw material (cedar) treated at a steam pressure of 3.5 MPa (243 °C) and a steaming time of 5 min to convert into useful products.
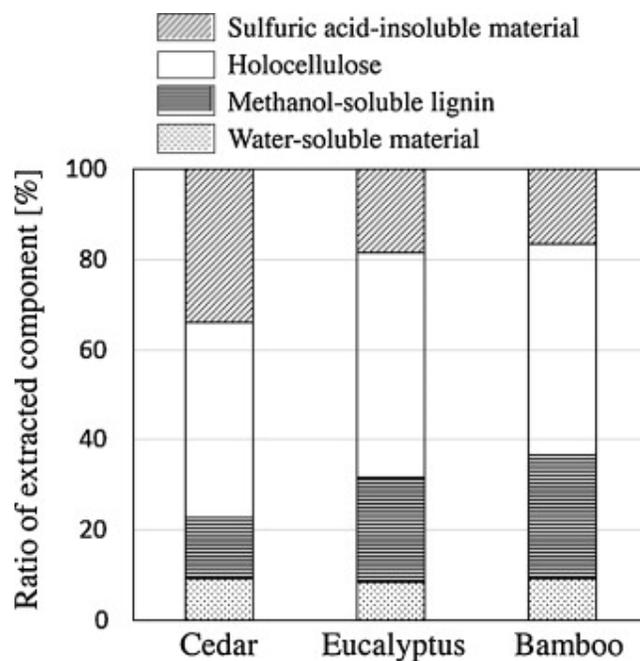
Figure 11: Comparison of extracted components from steam-exploded cedar, eucalyptus, and bamboo treated at a steam pressure of 3.5 MPa and a steaming time of 5 min.
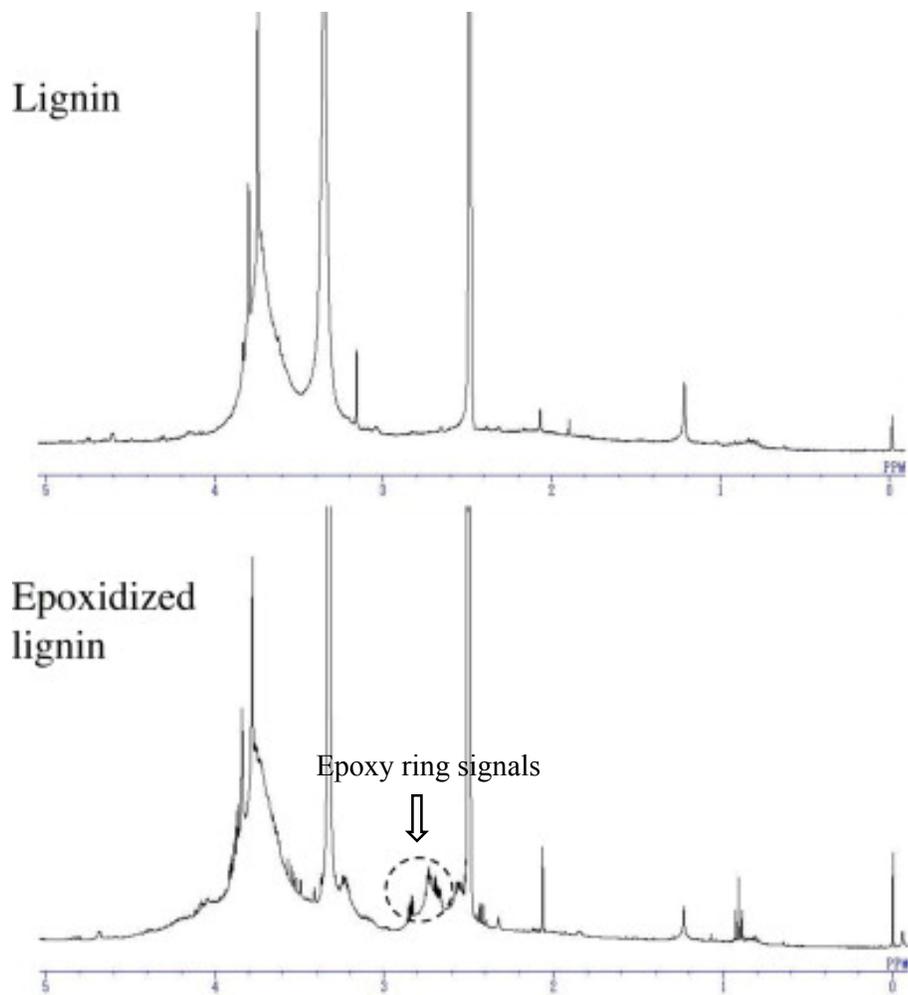
Figure 12: ^{1}H NMR Spectra of eucalyptus lignin and epoxidized eucalyptus lignin.
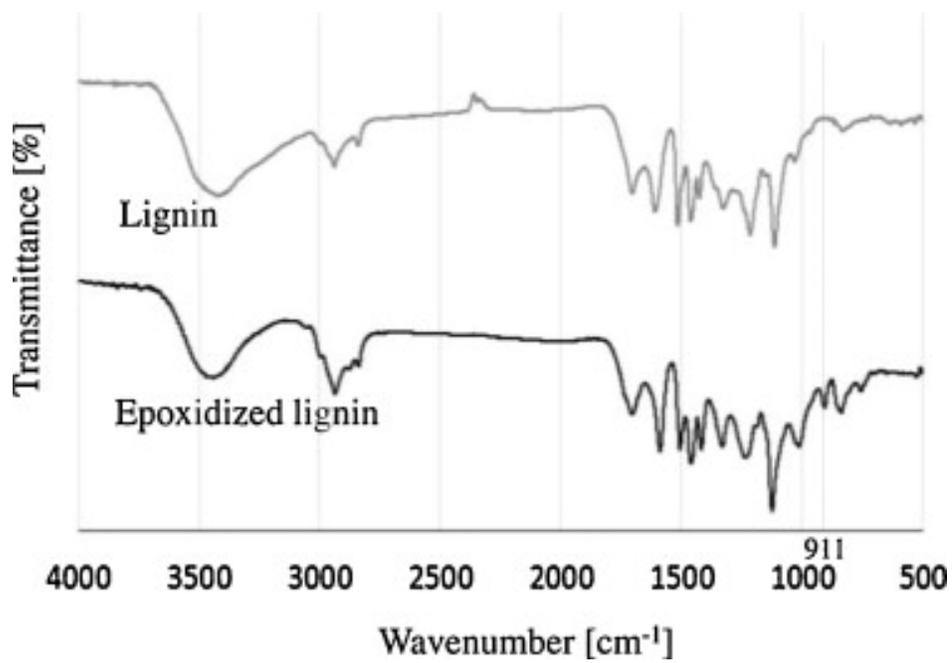
Figure 13: FT-IR spectra of eucalyptus lignin and epoxidized eucalyptus lignin.
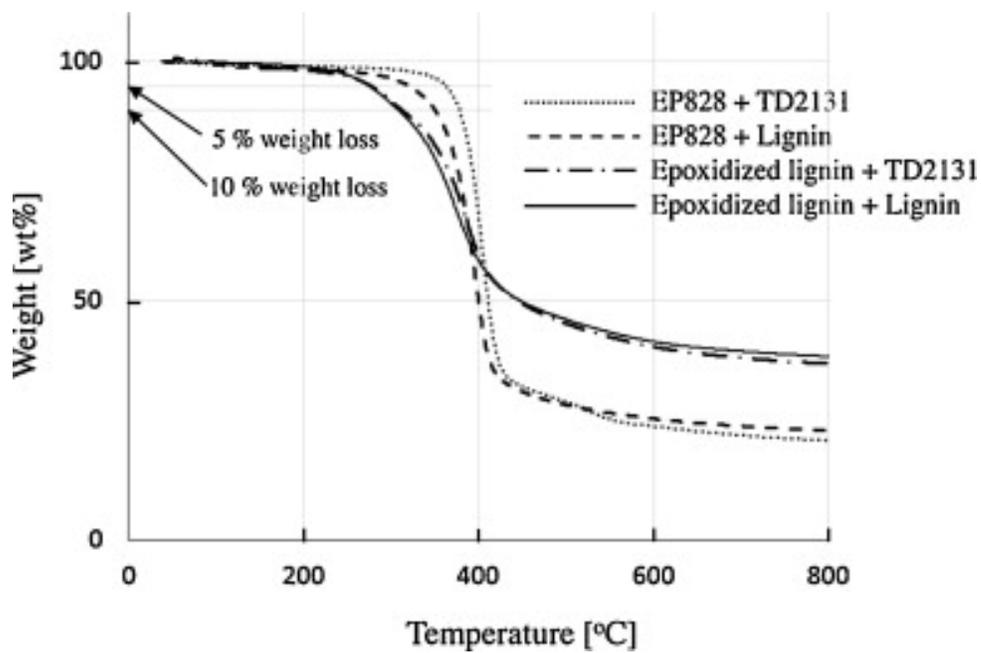
Figure 14: Thermogravimetric (TGA) profiles of cured epoxy resins. Eucalyptus lignin was used as a raw material in this experiment.

Table 4: Solubility of various lignins

Samples	Solvents			
	Tetrahydrofuran	Methanol	Epichlorohydrin	Water
Lignin (Alkaline), Tokyo Chem. Ind. Co.Ltd.	×	×	×	○
Lignin (Dealkaline), Tokyo Chem. Ind. Co.Ltd.	×	△	×	△
Sodium Ligninsulfonate, Tokyo Chem. Ind. Co. Ltd.	×	△	×	○
Lignin (Hydrolytic), Sigma-Aldrich Japan K. K.	△	△	△	△
Lignin, Kanto Chem. Co.Ltd.	×	△	×	○
Lignin (Alkaline), Nacalai Tesque, Inc.	×	×	×	○
Lignin extracted from cedar in this work (Methanol-soluble lignin)	○	○	○	×

○: Soluble, △: Slightly soluble, ×: Nearly insoluble

Table 5: Characteristics of lignin extracted from various steam- exploded plant biomass.

Sample	Purity (%)	Weight-average molecular weight	Hydroxyl equivalent (g/eq)
Cedar	99.1	1330	115
Eucalyptus	99	1400	115
Bamboo	99.2	1600	118

Table 6: Epoxy resin yield and epoxy equivalent of resin synthesized from bisphenol A and lignin extracted from various steam-exploded plant biomass.

Sample	Epoxy resin yield (%)	Epoxy equivalent (g/eq)
Bisphenol A	70	172
Cedar	63.4	337.5
Eucalyptus	66.9	342.5
Bamboo	68.2	345.4

Table 7: Thermal characteristics of cured epoxy resins.

Epoxy resin	Curing agent	Td_5 (°C)[a]	Td_{10} (°C)[b]	Char yield (%)[c]	Char yield (%)[d]	Biomass content (%)[e]
EP828	TD2131	361	378	23.7	20.7	0
	Lignin (Cedar)	326	363	24.2	22.5	34.2
EP828	Lignin (Eucalyptus)	319	349	25.2	22.8	39.5
	Lignin (Bamboo)	315	351	24.5	22	35.4
Epoxidized lignin (Cedar)		293	336	44.1	40.6	63.3
Epoxidized lignin (Eucalyptus)	TD2131	275	311	40.3	36.7	62.8
Epoxidized lignin (Bamboo)		266	313	36.6	33.1	64.7
Epoxidized lignin (Cedar)	Lignin (Cedar)	296	329	44.1	40.9	88.2
Epoxidized lignin (Eucalyptus)	Lignin (Eucalyptus)	274	307	41.3	38.3	86.1
Epoxidized lignin (Bamboo)	Lignin (Bamboo)	259	298	32.8	29	87.3

[a] Temperature of 5% weight loss under N_2 as given by TGA

[b] Temperature of 10% weight loss under N_2 as given by TGA.

[c] Char yield at 600 °C under N_2 as given by TGA.

[d] Char yield at 800 °C under N_2 as given by TGA.

[e] Biomass content in epoxy resin calculated according to the resin yield.

RESEARCH ACHIEVEMENT

Peer - reviewed papers

1. <u>Sunita Basnet</u>, Masaya Otsuka, Chizuru Sasaki, Chikako Asada, Yoshitoshi Nakamura. Functionalization of the active ingredients of Japanese green tea (Camellia sinensis) for the synthesis of bio-based epoxy resin. Journal of Industrial Crops and Products, 73 (2015), 63–72.

2. Chikako Asada, <u>Sunita Basnet</u>, Masaya Otsuka, Chizuru Sasaki, Yoshitoshi Nakamura. Epoxy resin synthesis using low molecular weight lignin separated from various lignocellulosic materials. International Journal of Biological Macromolecules, 74 (2015), 413–419.

Presentation

3. <u>Sunita Basnet</u>, Masaya Otsuka, Chizuru Sasaki, Chikako Asada, Yoshitoshi Nakamura. Catechin from Green tea; a Potential Candidate for Biobased Epoxy Resin. International Forum on Advanced Technologies, Tokushima, Japan, 2015.3.9, page 86.