



저작자표시-비영리-변경금지 2.0 대한민국

이용자는 아래의 조건을 따르는 경우에 한하여 자유롭게

- 이 저작물을 복제, 배포, 전송, 전시, 공연 및 방송할 수 있습니다.

다음과 같은 조건을 따라야 합니다:



저작자표시. 귀하는 원저작자를 표시하여야 합니다.



비영리. 귀하는 이 저작물을 영리 목적으로 이용할 수 없습니다.



변경금지. 귀하는 이 저작물을 개작, 변형 또는 가공할 수 없습니다.

- 귀하는, 이 저작물의 재이용이나 배포의 경우, 이 저작물에 적용된 이용허락조건을 명확하게 나타내어야 합니다.
- 저작권자로부터 별도의 허가를 받으면 이러한 조건들은 적용되지 않습니다.

저작권법에 따른 이용자의 권리는 위의 내용에 의하여 영향을 받지 않습니다.

이것은 [이용허락규약\(Legal Code\)](#)을 이해하기 쉽게 요약한 것입니다.

[Disclaimer](#)

A THESIS FOR THE DEGREE OF MASTER SCIENCE

**Sequential fractionation of lignin macromolecules  
with organic solvents and investigation of their  
potentials for lignin-PLA composites**

유기용매를 이용한 리그닌 분획 및  
분획물의 리그닌-PLA 복합재로써 활용 가능성 탐색

By Shin Young Park

Program in Environmental Material Science

Graduate School

Seoul National University

February, 2017

A THESIS FOR THE DEGREE OF MASTER SCIENCE

**Sequential fractionation of lignin macromolecules  
with organic solvents and investigation of their  
potentials for lignin-PLA composites**

유기용매를 이용한 리그닌 분획 및  
분획물의 리그닌-PLA 복합재료써 활용 가능성 탐색

By Shin Young Park

Major Professor: Hye Jung Youn

Program in Environmental Material Science

Graduate School

Seoul National University

February, 2017

# Abstract

## **Sequential fractionation of lignin macromolecules with organic solvents and investigation of their potentials for utilization as lignin-PLA composites**

Shin Young Park  
Program in Environmental Material Science  
Graduate School  
Seoul National University

Milled wood lignin (MWL), organosolv lignin (OL), and soda lignin (SL) were sequentially fractionated with ethyl acetate (F1), 2-butanone (F2), methanol (F3), acetone (F4), and dioxane/water (95:5 v/v, F5). Yields of the five MWL fractions were 11.7%, 11.7%, 15.3%, 11.8%, and 49.6%, and yields of OL fractions were 26.2%, 26.1%, 18.7%, 3.7%, and 25.4% where yields of SL fractions were 30.1%, 25.5%, 24.7%, 2.0%, 11.2%, and 6.5% of insoluble fraction (INS) was remained. GPC analysis showed that the molecular weights of lignin fractions increased from F1 to F5. The average molecular weight of F1 ranged from 1000 to 2400 Da. whereas that of F5 was above 10000 Da revealing that molecular weight of fractions increased from F1 to F5. According to functional group analysis, the contents of phenolic hydroxyl groups and methoxyl groups decreased gradually with increasing molecular weight. DFRC analysis revealed that the higher molecular weight fractions yielded larger amounts of DFRC monomers indicating that later fractions contain more aryl ether linkages than earlier fractions. According to Py-GC/MS analysis, main pyrolysis products of each fraction were analysed.

S/G ratios obtained by DFRC and Py-GC/MS analysis showed difference since condensed structure of lignin might bias the result of DFRC. TG/DTG analysis suggested that the low molecular weight fractions generally have lower thermal stability than other fractions due to their high content of functional groups.

Native SL and SL fraction were individually grafted with L-lactide via ring-opening polymerization to produce lignin-grafted-poly(L-lactide) (lignin-g-PLLA). Conversion ratio of each fraction was calculated by  $^1\text{H}$  NMR and revealed that SL F1 which contains the largest amount of hydroxyl groups had the highest conversion ratio of 91.2% while SL F5 showed the lowest value of 88.3%. However, SLF1-g-PLLA showed the lowest molecular weight ( $M_n$ ) where that of SLF5-g-PLLA was the highest indicating that SLF5-g-PLLA had the longest PLLA chain length. According to DSC analysis, it was revealed that SL-g-PLLA had the highest glass transition temperature due to its structural complexity. Surface characterization using scanning electron microscope suggested that surface of lignin grafted with PLLA had is smoother than that of native lignin, while SL F1, F3, and F5 had more smoother surface than SL and SLINS grafted with PLLA. Each copolymer was mixed with PLA 2002D to manufacture a lignin-PLA composite. Tensile strengths of composites were varied by chain lengths and surface properties of copolymers. In case of tensile modulus, the chain length of copolymer affected mainly.

**Key words: lignin, solvent fractionation, Functional groups, lignin application, PLA grafting, lignin copolymer**

**Student number: 2015 - 21503**

# Contents

<b>1. Introduction</b> .....	<b>1</b>
1.1. Lignin as an alternative to fossil fuel .....	<b>1</b>
1.2. Obstacles to lignin utilization .....	<b>3</b>
1.3. Lignin solvent fractionation .....	<b>4</b>
1.4. Lignin-grafted-poly lactide (PLA) .....	<b>6</b>
1.4. Objectives .....	<b>7</b>
<b>2. Literature review</b> .....	<b>8</b>
2.1. Lignin solvent fractionation .....	<b>8</b>
2.2. Factors effect on lignin application .....	<b>10</b>
2.3. Utilization of fractionated lignin .....	<b>12</b>
2.4. Utilization of lignin into lignin-grafted-poly lactide (PLA) copolymer	<b>14</b>
<b>3. Materials and methods</b> .....	<b>15</b>
3.1. Materials .....	<b>15</b>
3.2. Lignin preparation.....	<b>16</b>
3.3. Lignin solvent fractionation .....	<b>17</b>
3.4. Structural analysis of fractionated lignin .....	<b>19</b>
3.4.1. Gel permeation chromatography (GPC) .....	<b>19</b>
3.4.2. Nuclear magnetic resonance spectrometry (NMR) .....	<b>19</b>
3.4.3. Methoxyl group contents analysis .....	<b>19</b>

3.4.4. DFRC analysis .....	20
3.5. Thermal analysis of fractionated lignin .....	21
3.5.1. Pyrolysis – Gas chromatography / Mass spectrometry (Py-GC/MS) .....	21
3.5.2. Thermogravimetric analysis (TGA) .....	21
3.6. Application of lignin fractions: Lignin-PLA grafting .....	22
3.6.1. Synthesis of Lignin-graft-poly(L-lactide) .....	22
3.6.2. Analysis of lignin-g-PLA.....	24
3.6.2.1. Analysis of conversion ratio of lignin-g-PLLA by <sup>1</sup> H NMR .....	24
3.6.2.2. Analysis of thermal properties of lignin-g-PLLA .....	24
3.6.2.3. Investigation of surface of lignin-g-PLLA .....	24
3.6.2.4. Investigation of mechanical properties of lignin-g-PLLA .....	25
<b>4. Results and discussion.....</b>	<b>26</b>
4.1. Yields of lignin fractions .....	26
4.2. Molecular weight distributions of lignin fractions .....	28
4.3. Determination of functional group contents .....	30
4.4. Determination of S/G ratios of lignin fractions by DFRC .....	32
4.5. Pyrolytic analysis of lignin fractions by Py-GC/MS .....	34
4.6. Thermal decomposition characteristics of lignin fractions .....	40
4.7. Analyses of lignin-grafted-PLLA copolymers .....	45
4.7.1. Features of grafted PLLA onto lignin .....	45

4.7.2. Thermal properties of lignin-g-PLLA .....	48
4.7.3. Surface characterization of lignin-g-PLLA .....	51
4.7.4. Mechanical properties of lignin-g-PLLA .....	53
<b>5. Conclusion .....</b>	<b>57</b>
<b>6. References .....</b>	<b>59</b>

## List of Tables

<b>Table 1.</b> Chemical and structural properties of lignin fraction .....	<b>27</b>
<b>Table 2.</b> Quantitative analysis of DFRC products of lignin fractions and their S/G ratios analyzed by DFRC .....	<b>33</b>
<b>Table 3.</b> Pyrolysis products from lignin fractions of MWL using GC/MS analysis .....	<b>36</b>
<b>Table 4.</b> Pyrolysis products from lignin fractions of OL using GC/MS analysis .....	<b>37</b>
<b>Table 5.</b> Pyrolysis products from lignin fractions of SL using GC/MS analysis .....	<b>38</b>
<b>Table 6.</b> Comparison of S/G ratios determined by DFRC and Py-GC/MS analysis .....	<b>39</b>
<b>Table 7.</b> The yield of char residue, maximum degradation temperature, and maximum degradation rate of lignin fractions obtained from TG/DTG analysis .....	<b>44</b>
<b>Table 8.</b> Conversion ratios of lignin-g-PLLA .....	<b>47</b>
<b>Table 9.</b> Glass transition temperatures of lignin-g-PLLAs determined by DSC .....	<b>49</b>
<b>Table 10.</b> Tensile strength and modulus of lignin-g-PLLA .....	<b>56</b>

## List of Figures

<b>Fig. 1.</b> Scheme of lignin solvent fractionation .....	<b>5</b>
<b>Fig. 2.</b> Process of lignin solvent fractionation .....	<b>18</b>
<b>Fig. 3.</b> Reaction of synthesis of lignin-g-PLLA via ring-opening polymerization .....	<b>23</b>
<b>Fig. 4.</b> GPC curves of (a) MWL, (b) OL, and (c) SL fractions .....	<b>29</b>
<b>Fig. 5.</b> TG thermograms of lignin fractions: (a) MWL, (b) OL, and (c) SL .....	<b>42</b>
<b>Fig. 6.</b> DTG thermograms of lignin fractions: (a) MWL, (b) OL, and (c) SL .....	<b>43</b>
<b>Fig. 7.</b> DSC curves of lignin-g-PLLA. Red-dotted square indicates the glass transition temperature area .....	<b>50</b>
<b>Fig. 8.</b> SEM images of SL and their fractions grafted with PLLA. (a, b) original SL, (c, d) SL-g-PLLA, (e, f) SLF1-g-PLLA, (g, h) SLF3-g-PLLA, (i, j) SLF5-g-PLLA, and (k, l) SLINS-g- PLLA. ....	<b>52</b>

# 1. Introduction

## 1.1. Lignin as an alternative to fossil fuel

After the Industrial Revolution, fossil fuels such as coal and petroleum became the most important resources for the human. Nowadays, fuel, electricity, and even materials are mostly derived from these fossil fuels. However, as usage of fossil fuels increased, some problems like global warming, oil price fluctuation, and concern about depletion of fossil fuels came up. To overcome these problems, alternative energy has been got attention. Now sustainable energy include biomass, solar power, and wind power are regarded as energy sources for the future and many efforts have been doing to replace fossil fuels with them. Among them, biomass is now noticed as an alternative energy source to alter fossil fuels. Biomass is usually composed of three major compounds, cellulose, hemicellulose, and lignin. Each of them can be separated from biomass and go into bioenergy, biochemical, biocomposites, and so on.

Lignin, the second most abundant biopolymer on Earth, constitutes about 20~30% of woody biomass. It is composed of three major phenyl propanoid units such as *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These three units are combined heterogeneously and complicatedly via some kinds of ether and carbon-carbon linkages like  $\beta$ -O-4,  $\alpha$ -O-4,  $\beta$ - $\beta$ , 5-5, and so on (Achyuthan et al., 2010; Yaku et al., 1981). In plants, lignin makes complexes with cellulose and hemicellulose (LCC) and these linkages are very hard to cleavage. Thus, it is difficult to isolate pure lignin from plant cell walls. Commercial lignin is usually produced from the pulping and bioethanol

industries and about 50 million tons of lignin were produced in 2010.

Lignin is expected to applicate for various fields. As lignin has a phenolic group, fuels and chemicals like benzene, toluene, xylen, and phenol can be obtained from lignin. Lignin also has potential to alter petroleum-derived materials such as plastics and carbon materials due to its thermoplasticity and high carbon content. Moreover, special properties of lignin like UV-resistant, anti-oxidant ability, and thermal stability also give lignin possibilities to utilization of lignin as a blender, filler, antioxidant, and many other materials.

## **1.2. Obstacles and modification for lignin utilization**

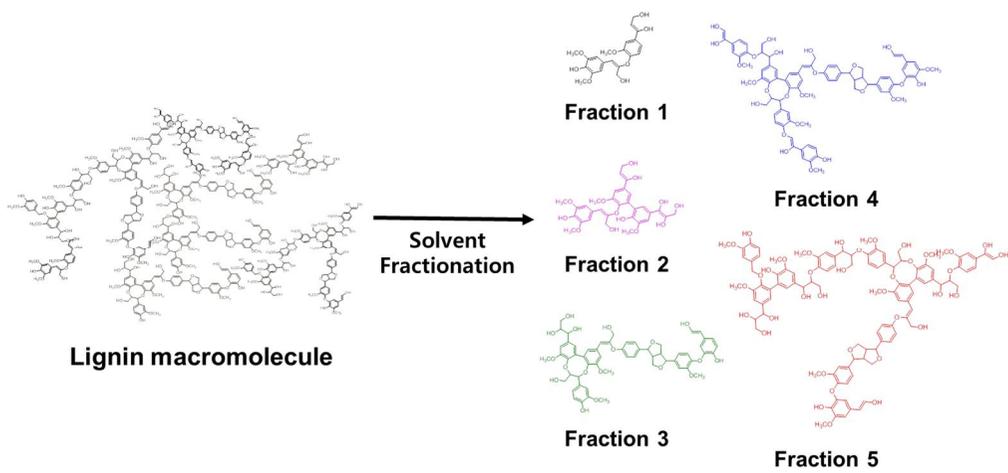
However, although lignin has high potential to be utilized as value-added products, just small amount of lignins are now commercially used and most of them are burned for producing heat energy required in the pulping process (Ragauskas et al., 2006; Zhang et al., 2011). This difficulty is attributed to some undesirable properties of lignin. As lignin has very complex and heterogeneous structures and also has very wide molecular weight range, it is very difficult to obtain lignin as a monomer or a homogeneous molecule. In addition, low solubility of lignin in organic solvents also makes lignin difficult to be utilized.

To overcome these obstacles, many studies have been performed. Lignin depolymerization can convert the complex structure of lignin into small molecules by pyrolysis or gasification or hydrogenolysis for fuels, chemicals, and further applications (Pandey & Kim, 2011). Other researches are interested in improving homogeneity of lignin and reducing its complexity with various methods such as organic solvent fractionation (Li et al., 2012; Thring et al., 1996; Wang et al., 2010), gel permeation chromatography (Kirk et al., 1969), and ultrafiltration (Toledano et al., 2010; Wallberg et al., 2003).

### 1.3. Lignin solvent fractionation

Lignin solvent fractionation is a method that fractionates lignin into some fractions using several kinds of organic solvents. Schuerch found that the ability of solvents to dissolve lignin can be varied by their hydrogen bonding capacity ( $\Delta\mu$ ) and Hildebrand solubility parameter ( $\delta$ ) (Schuerch, 1952). According to Schuerch, solvents which have  $\Delta\mu$  values of 0.14 or higher and  $\delta$  values around 11 are good lignin solvents. He also found that low molecular weight lignin can be solubilized in wider range of solvents. Thus, by using various organic solvents sequentially, lignin can be fractionated into several fractions with specific molecular weight distributions and become more homogeneous (Fig. 1). In addition, each lignin fraction obtained by sequential solvent fractionation may have different characteristics on functional groups and thermal stabilities. Thus, each lignin fraction is expected to have separate application fields which their own properties can act on properly.

There are many kinds of industrial lignins and they have different solubility to organic solvents. According to previous studies, various kinds of lignins include kraft lignin, Alcell lignin, kraft-AQ lignin and organosolv lignin were fractionated and their structural and thermal properties were investigated (Li et al., 2012; Mörck et al., 1986; Thring et al., 1996; Wang et al., 2010; Yoshida et al., 1987). However, previous researches were focused on just one kind of lignin and each study used different fractionation method. Moreover, compared to lignin fractionation study, studies on the utilization of fractionated lignin have not been performed much. Therefore, not only study on the features of fractionated lignin but also study on further application of lignin fraction should be performed.



**Fig. 1.** Scheme of lignin solvent fractionation

## **1.4. Lignin-grafted-poly lactide (PLA)**

Poly lactide (PLA) is a promising bioplastic that is already commercialized. However, PLA has some undesirable properties such as brittleness, low thermal stability, and low UV-resistance. Due to these drawbacks, PLA could not yet replace commercial petroleum-derived plastics despite of its sustainable and biodegradable properties. Thus, many researches were performed to improve its properties by blending or grafting other materials with PLA. One of methods to reinforce PLA is grafting PLA onto lignin. Since lignin has good thermal stability and high UV-resistance, by attaching the chain of PLA on hydroxyl groups of lignin, properties of PLA composites are expected to be improved. In addition, AS grafted copolymer shows better interfacial interaction than simply blended composites, decrease of mechanical strengths of composites might be prevented. Previous studies revealed that grafting poly(L-lactide) onto lignin via ring opening polymerization can enhance not only its thermal and UV stabilities but also its mechanical properties (Chung et al., 2013; Zong et al., 2016).

## 1.5. Objectives

Lignin has a huge potential to substitute fossil fuels completely and many researches were performed to utilize lignin as value-added products into various fields. However, until now just few portion of lignin has been used commercially. Heterogeneous and complex structure of lignin is regarded as the main obstacle for lignin utilization. Thus, to utilize lignin more valuably, process of lignin modification is needed. Among the methods homogenizing lignin, lignin solvent fractionation can homogenize lignin into several fractions through simple, low-energy-consuming process. Besides, lignin fractions obtained from solvent fractionation have different properties; therefore each of them can be applied in appropriate fields respectively.

In this study, three kinds of lignin were fractionated (milled wood lignin, organosolv lignin, and soda lignin) sequentially with five kinds of organic solvents (ethyl acetate, 2-butanone, methanol, acetone, dioxane/water (95:5 v/v)), and comparison of the structural and thermal properties of those fractions were conducted. In addition, to investigate the potentials for application of fractionated lignins, lignin fractions were grafted with L-lactide, and the evaluations of characteristics of these copolymers were performed.

The aim of this study was (1) to compare the influence of solvent fractionation on the three different kinds of lignin, (2) to obtain homogeneous and narrow molecular weight range lignin fractions, (3) to analyse the structural and thermal properties of those lignin fractions for understanding lignin complex structures and their further applications, and (4) to utilize lignin fractions as a lignin-grafted-poly lactide copolymer to suggest the possibility of application of lignin fractions.

## 2. Literature review

### 2.1. Lignin solvent fractionation

Schuerch (1952) reported that solubility of lignin into organic solvents is affected by hydrogen bonding capacity ( $\Delta\mu$ ) and Hildebrand solubility parameter ( $\delta$ ). According to his study, solvents having  $\Delta\mu$  value higher than 0.14 and  $\delta$  value around 11 show higher solubility of lignin. He also evaluated the ability of various solvents to dissolve lignin.

From then on, many researches were performed to fractionate lignin with solvents. R. Mörck et al. fractionated kraft lignin successively with five kinds of organic solvents and analysed their structural properties. They analysed functional groups with  $^{13}\text{C}$ -NMR and molecular weight distribution and showed that lower molecular weight fractions have higher solubility and higher contents of functional groups such as phenolic hydroxyl groups and methoxyl groups (Mörck et al., 1986). Yoshida et al. also found that thermal stability and glass transition temperature of kraft lignin was found to increase with increasing molecular weight (Yoshida et al., 1987).

Thring et al. (1996) fractionated Alcell lignin into three fractions by sequential solvent extraction with organic solvents of increasing hydrogen-bonding capacity (ether and methanol). They showed that 27% of Alcell lignin was found to have a very low molecular weight ( $M_w = 714 \text{ g/mol}$ ) fraction soluble in ether and this fraction had a lower polydispersity index but a higher contents of G units than higher molecular weight fractions.

According to Wang et al. (2010), kraft-AQ pulping lignin was also sequentially fractionated by five organic solvent extractions. As same as previous studies, the average molecular weight and polydispersity of each

lignin fraction increased with its hydrogen-bonding capacity. They also reported that the ratio of the non-condensed G/S units, content of  $\beta$ -O-4 linkages, and thermal stability increased as lignin molecular weight increased.

Although solvents and fractionation methods in these studies were different, they showed that lower molecular weight lignin fraction has higher solubility to solvents, higher functional group contents, higher contents of  $\beta$ -O-4 linkages, and lower thermal stability than higher molecular weight fraction.

## 2.2. Factors effect on lignin application

By solvent fractionation of lignin, lignin fractions which have some different characteristics on molecular weight, functional groups, and thermal properties can be obtained and these properties have very important roles in lignin application. Thus, these fraction are able to utilize in separate field where property of each fraction is suitable. Therefore, before utilizing lignin fractions, studies related to factors effect on lignin application should be performed to applicate lignin fractions in appropriate field.

Lignin hydroxyl groups play an important role when lignin reacts with other molecules. According to Duval and Lawoko, lignin hydroxyl groups can initiate the ring-opening polymerization of  $\epsilon$ -caprolactone (CL) and produce lignin-grafted-polycaprolactone (PCL) (Duval & Lawoko, 2014). Laurichesse and Avérous synthesized soda lignin-grafted-PCLs with a different CL/OH molar ratios and showed that when the CL/OH ratio was 5, the products was flexible and didn't have a crystalline structure while samples with a CL/OH ratios higher than 5 form a semi-crystalline structure and showed brittleness (Laurichesse & Avérous, 2013).

Polyurethane derived from lignin is one of the most studied fields of lignin application. Yoshida et al. syththesized polyurethane films with kraft lignin-polyether triol and reported that high molecular weight lignin which bearing higher number of hydroxyl groups yields polyurethane with higher crosslinking density (Yoshida et al., 1987). The similar results were also reported by Kelley et al. (Kelley et al., 1989) and Evtuguin et al. (1998) (Evtuguin et al., 1998).

Lignin phenol groups are also known for their antioxidant properties due to their ability to scavenge free radicals. Gregorová et al. (2005) utilized

lignin as a stabilizer in polypropylene and found that lignin having low molecular weight and narrow polydispersity showed the stabilization effect in polypropylene and recycled polypropylene matrices (Gregorová et al., 2005).

Lignin melt spinnability for carbon fiber is highly dependent on the structure of lignin. Kadla et al. revealed that low molecular weight lignin can be spinnable easily. They also showed that lignin having rather linear structure can also be melt spun easier than crosslinked lignin (Kadla et al., 2002). According to Baker, lignin bearing additional methoxyl groups and narrow molecular weight distribution is more amenable to melt spinning for lignin carbon fiber (Baker, 2010).

### **2.3. Utilization of fractionated lignin**

Some researches utilized fractionated lignin into some fields in practice and according to these researches, each fraction showed the different results when utilized. Thus, it can be said that lignin fractionation can improve possibilities of lignin to utilize in real fields.

Vanderlann and Thring (1998) synthesized lignin-derived polyurethane films using three Alcell lignin fractions and revealed that films derived from each fraction showed different properties. According to their study, the crosslinking density was increased with molecular weight of lignin, thus, strong polyurethanes were produced from the high molecular weight fraction while medium molecular weight fraction based polyurethane appeared to be tougher and more flexible (Vanderlaan & Thring, 1998).

Gosselink et al. (2010) fractionate four technical lignin with successive organic solvent extraction and modeling by principle component analysis (PCA) was performed to predict the application potential of lignins for binder production. They reported that softwood kraft lignin containing high level of free ortho ring positions and condensed structures showed the highest potential for use as wood adhesive and medium molar mass fractions of grass soda lignin also can be able to use as a plywood adhesive (Gosselink et al., 2010).

Yue et al. (2012) divided soda lignin into three fractions by sequential solvent extraction and those fractions were blended with poly (vinyl chloride) (PVC). The lignin fraction with low molecular weight could be dispersed more uniformly in PVC matrix and thus it accelerates the plasticization of blend. However, high molecular weight lignin fraction improved the maximum decomposition temperature of blend. Unfractionated native soda

lignin decreased mechanical properties of the blend due to its heterogeneity (Yue et al., 2012).

Li et al. (2012) fractionated bamboo organosolv lignin with four organic solvents and analysed their structural, thermal, and antioxidant ability properties. They revealed that with increasing the dissolving capacity of solvent, the contents of functional groups were decreased and lower molecular weight fraction which has higher contents of phenolic hydroxyl groups had a high radical scavenging index which means having good property for antioxidant (Li et al., 2012).

## 2.4. Utilization of lignin as lignin-PLA composites

Lignin has a potential to improve thermal stability and UV-resistance of PLA. Thus, some researches were performed to investigate the effect of lignin on the properties of PLA composites.

Li et al. (2003) blended dried lignin and purified PLLA in a different ratios. They found that glass transition temperature of PLA/lignin decreased as the content of lignin in the blends increased. It was also revealed that when contents of lignin was more than 20%, the thermal degradation of PLLA was accelerated. In a tensile test, tensile strength and modulus of composites were decreased as lignin contents increased (Li et al., 2003).

Chung et al. (2013) grafted L-lactide with Indulin AT lignin to produce the lignin-lactide copolymer. L-lactide was grafted onto hydroxyl groups existing in lignin macromolecule and formed poly(L-lactide) (PLLA) chain via ring-opening polymerization (ROP). Some properties of lignin-lactide copolymer were estimated, and they showed that lignin played a role as enhancing UV absorption and reducing brittleness of PLA (Chung et al., 2013).

With reference their study, Zong et al. (2016) combined biobutanol lignin (BBL) and L-lactide via ROP towards BBL-graft-PLLA copolymer. They characterized properties of copolymer and revealed that molecular weight of copolymer can be tunable by manipulating the mass ratio of BBL and L-lactide. In addition copolymer film showed good absorption in the UV region but high transparency in the visible light region (Zong et al., 2016).

## **3. Materials and methods**

### **3.1. Materials**

As raw materials, milled wood lignin (MWL) and organosolv lignin(OL) extracted from yellow poplar wood (*Liriodendron tulipifera*) and soda lignin (SL) purchased from Granit Research and Development SA. Ethyl acetate, methanol, acetone, and dioxane used in this study were purchased from Daejung chemicals & Metals Co. Ltd. and 2-Butanone was purchased from Sigma Aldrich.

L-lactide purchased from Tokyo chemical industry Co. LTD. and triazabicyclodecene (TBD) purchased from Sigma Aldrich was used for grafting copolymers.

### 3.2. Lignin preparation

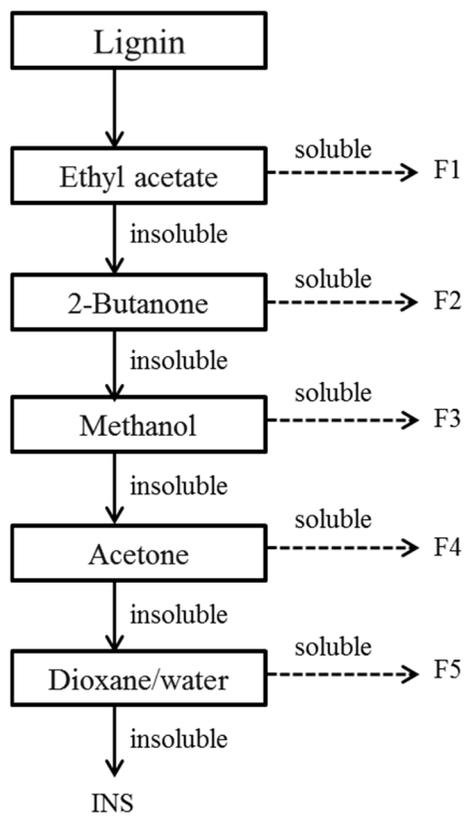
Milled wood lignin was extracted by Björkman's method (Björkman, 1956). 100 g of yellow poplar wood milled in a size of 0.5 mm was put into 1000 mL of ethanol/toluene (1:1 v/v) and stirred for 48 hours to eliminate extractives. After stirring, solvent was removed with vacuum filtration and the sample was dried for 24 h. Dried sample was ground finely for 48 hours with rotary ball miller for 120 h and was extracted twice with dioxane/water (95:5 v/v) for 24 h. Dioxane/water was evaporated completely with rotary evaporator and remained solute was dissolved into 100 mL of acetic acid, precipitated in 1000 mL of D.I water, centrifuged, and freeze-dried. Dried powder was dissolved in 30 mL of 1,2-dichloroethane/ethanol (2:1 v/v), precipitated in 1000 mL of diethyl ether, centrifuged, and freeze-dried again.

Organosolv lignin was extracted with ethanol / D.I water (1:1 v/v) solvent at 170 °C for 2 h and precipitated with D.I water according to the method by Hewson et al. (Hewson et al., 1941).

Soda lignin was purchased from Grait Research and Development SA which was generated from the soda pulping process of wheat straw and sarkanda grass.

### **3.3. Lignin solvent fractionation**

In this study, lignin solvent fractionation was conducted with five kinds of organic solvents which are ethyl acetate, 2-butanone, methanol, acetone, and dioxane/water (95:5 v/v) in order of increasing lignin solubility. 5 g of each lignin was dissolved into 100 mL of ethyl acetate and stirred for 2 h with magnetic bar at room temperature. After stirring, solution was filtered with 2G4 glass filter to separate filtrate and solid residue. Filtrate was evaporated by rotary evaporation completely for calculating yield and re-dissolved into 3~5 mL solvent. Then, it was precipitated with D.I water, centrifuged, and freezing-dried for obtain powder form fraction which was named F1. Solid residue remained on glass filter was dissolved into next organic solvent and process discribed above was repeated sequentially. Each fraction obtained from these process was named from F2 to F5 and finally remained insoluble residue was named INS. The overall process of solvent fraction is illustrated in Fig. 2



**Fig. 2.** Process of lignin solvent fractionation

### **3.4. Structural analysis of fractionated lignin**

#### **3.4.1. Gel permeation chromatography (GPC)**

Molecular weight distributions of lignin fraction was determined by GPC analysis. For GPC analysis, each lignin fraction was acetylated. 100 mg of each sample was dissolved in 2 mL of pyridine / acetic anhydride (1:1 v/v) solvent and reacted at 105 °C for 2 h. After reaction, solution was precipitated with D.I water, centrifuged, and freezing-dried. 2 ~ 3 mg of each acetylated lignin fraction was then dissolved into tetrahydrofuran (THF) and analyzed by GPC (Ultimate 3000, Thermo, USA).

#### **3.4.2. Nuclear magnetic resonance spectrometry (NMR)**

<sup>1</sup>H NMR was performed to investigate the contents of phenolic hydroxyl groups in each lignin fractions. 10 ~ 15 mg of lignin fractions was dissolved into 500 μL of DMSO-d<sub>6</sub> and stirred. Analysis was performed by 600 MHz High Resolution NMR Spectrometer (AVANCE 600, Bruker, Germany).

#### **3.4.3. Methoxyl group contents analysis**

The contents of methoxyl groups presented in lignin fractions were determined using a gas chromatography method by Baker (Baker, 1996). 30 mg of sample was dissolved into 4 mL of hydroiodic acid and reacted at 130 °C heating block for 30 min. After reaction, solution was cooled down to

room temperature and 3 mL of pentane and 200  $\mu$ L of ethyl iodide / pentane (1:9 v/v, internal standard) were added and shaken well. After the solution divided into two phases, supernatant layer was taken and put into GC vial for GC analysis. Agilent 7890 A gas chromatography (Agilent, USA) was used for analysis.

#### **3.4.4. DFRC analysis**

DFRC analysis of lignin fractions was performed to determine ratio of H/G/S units in each fraction. 20 mg of lignins and their fractions were dissolved in 4 mL of acetic acid/acetic bromide (92:8 v.v) and reacted at 70 °C for 2 h. Solvent was removed with rotary evaporator after reaction, 5 mL of dioxane/acetic acid/D.I water (5:4:1 v/v/v) and 100 mg of zinc dust were added and shaken for 30 min. Then it was put into fractional funnel, and 10 mL of methylene chloride, 10 mL of saturated ammonium chloride solution, and 50  $\mu$ L of internal standard (0.0137g tetracosane / 2 mL methylene chloride) were added. The mixture was acidified under pH 2 with 3 mL of 2M HCl and the layer of methylene chloride was collected. Extraction with 10 mL of methylene chloride was repeated and collected twice. Moistures in the collected layer were removed with anhydrous sodium sulfate, filtered, and rotary-evaporated. Remain solute was acetylated with 0.5 mL of pyridine and acetic anhydride and analyzed by GC/MS.

### **3.5. Thermal analysis of fractionated lignin**

#### **3.5.1. Pyrolysis – Gas chromatography / Mass spectrometry (Py-GC/MS)**

Py-GC/MS analysis was conducted to analyse pyrolysis products and determine H/S/G ratio of each fraction. 1 mg of each fraction was introduced into a quartz tube with a 2  $\mu\text{L}$  internal standard (1.3 mg of fluoranthene / mL in acetone). Each sample was then pyrolyzed at 600  $^{\circ}\text{C}$  with a 10  $^{\circ}\text{C}$  / ms heating rate in an inert atmosphere ( $> 99.9\%$  He) for 20 s using a CDS pyroprobe 200 (CDS Analytical Inc., Oxford, PA, USA). The released volatile products were analysed by gas chromatography (Agilent Technologies 7890A) and mass selective detector (Agilent Technologies 5975A).

#### **3.5.2. Thermogravimetric analysis (TGA)**

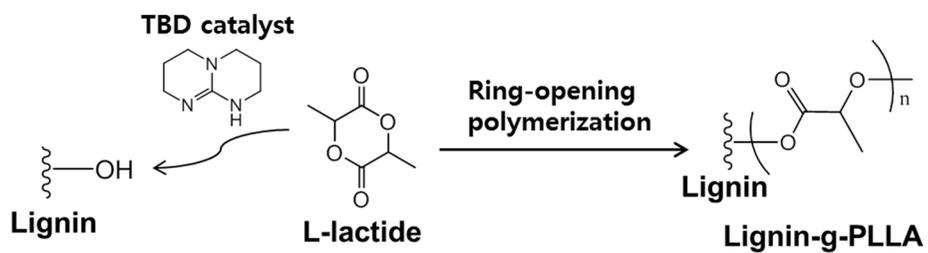
Thermal decomposition characteristic of each fraction was determined by TGA with TGA/DSC 3+ (Mettler Toledo, Switzerland). Sample was pre-dried at 105  $^{\circ}\text{C}$  oven for 24 h to minimize effect of moisture. Analysis was performed at a constant heating rate of 10  $^{\circ}\text{C}$  / min up to 800  $^{\circ}\text{C}$  while an inert atmosphere was maintained with a 50 mL / min of  $\text{N}_2$  flow.

### **3.6. Application of lignin fractions: Lignin-PLLA grafting**

To investigate the possibility to utilize lignin fractions into a specific field, fractionated lignins were grafted with L-lactide to produce lignin-grafted-poly(L-lactide) (lignin-g-PLLA). In this study, SL and its F1, F3, F5, and INS were used to make a copolymer.

#### **3.6.1. Synthesis of Lignin-graft-poly (L-lactide)**

Each lignin fraction was grafted with L-lactide by ring-opening polymerization (Fig. 3). 0.5 g of lignin fraction, 5 g of L-lactide, and 50 mg of triazabicyclodecene (TBD) catalyst were put into a vial. Vial was sealed and stirred at 130 °C for 4 h in a N<sub>2</sub> atmosphere. After the reaction, sample was dissolved into dichloromethane solution of acetic acid. It was then precipitated with methanol, centrifuged, and collected (Chung et al., 2013).



**Fig. 3.** Reaction of synthesis of lignin-g-PLLA via ring-opening polymerization

### **3.6.2. Analysis of lignin-g-PLA**

#### **3.6.2.1. Analysis of conversion ratio of lignin-g-PLLA by $^1\text{H}$ NMR**

$^1\text{H}$  NMR was performed to investigate the conversion ratio of lignin-g-PLLA. Each sample was dissolved in deuterated chloroform ( $\text{CDCl}_3$ ) for analysis. Analysis was performed by 600 MHz High Resolution NMR Spectrometer (AVANCE 600, Bruker, Germany).

#### **3.6.2.2. Analyses of thermal properties of lignin-g-PLLA**

Glass transition temperature ( $T_g$ ) of each copolymer sample was determined by DSC. 4~6 mg of samples were placed into standard aluminium pans and heated at a rate of 20  $^\circ\text{C}$  / min using DSC-Q1000 (TA Instrument, UK).

#### **3.6.2.3. Investigation of surface of lignin-g-PLLA**

Surface of each lignin-g-PLLA was investigated by scanning electron microscope (TM3030Plus, Hitachi High Technologies, Japan) at an accelerating voltage of 15kV.

#### **3.6.2.4. Investigation of mechanical properties of lignin-g-PLLA**

To investigate mechanical properties of copolymer, each lignin-g-PLLA and PLA 2002D were mixed in a ratio of 1:20. The mixed PLA/lignin-g-PLLA was then dissolved into chloroform and stirred for 15 hrs at the room temperature. After dissolving, solution was precipitated with isopropyl alcohol, centrifuged, and freeze-dried. Obtained PLA/lignin-g-PLLA was then used for tensile test according to ASTM D 638-10. Each sample was molded at 190 °C using an injection molding machine (Bautek Co., Korea) for making a tensile testing sample. Tensile test was then performed using the universal testing machine (Zwick Co., Germany). The space between the grips were 50 mm and test was served at a constant deformation speed of 5mm/min.

## 4. Result and Discussion

### 4.1. Yields of lignin fractions

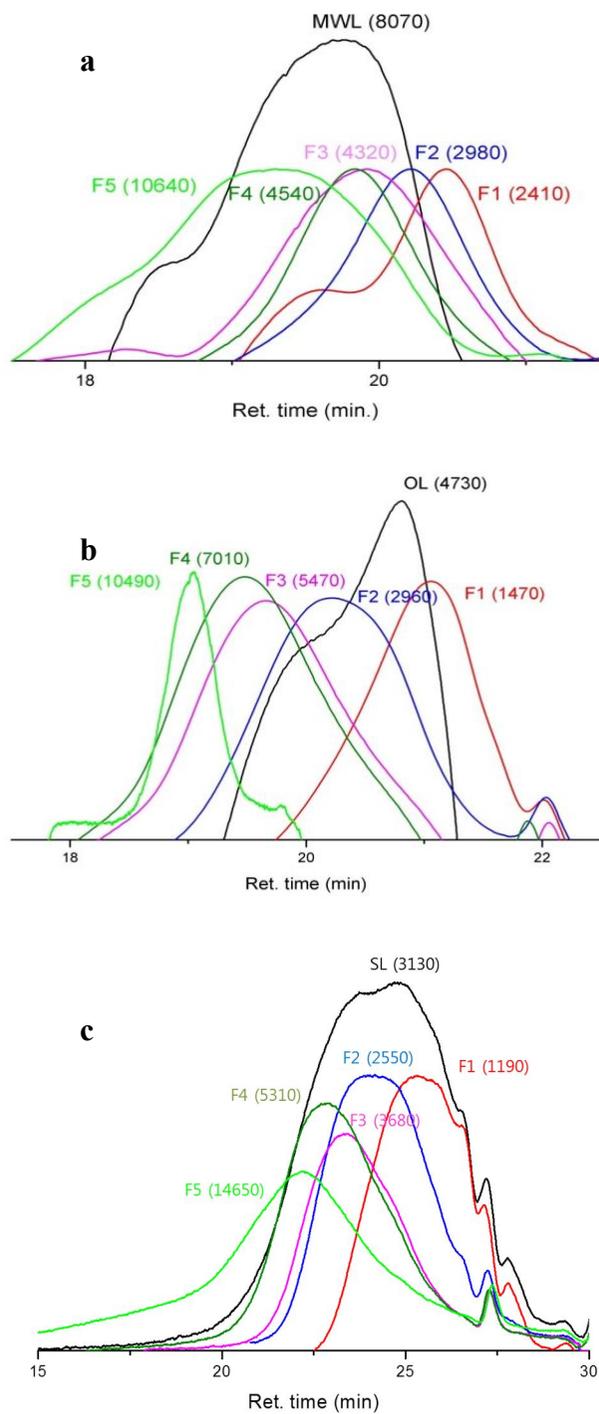
The yield of each fraction was calculated and shown in Table 1. MWL showed yields from F1 to F4 which were ranged from 11.7 % to 15.3 %, but relatively higher yield of F5 (49.6 %). Insoluble was not remained and this is because MWL was extracted with dioxane/water. In case of OL, F4 (3.7 %) had the lowest yield, while other fractions yielded from 18.7 % to 26.2 % and produced no residual insoluble. SL also showed low yield for F4 (2.0 %) while other fractions ranged from 11.2 % to 30.1 %. In addition, interestingly, SL also had insoluble fraction (INS) which portioned 6.5 %. Each lignin showed different yields of fractions because they have different structure and different solubility to solvents. Properties of solvent used in this study are likely to describe as below; ethyl acetate ( $\delta = 9.1$ ,  $\Delta\mu = 0.12$ ), 2-butanone ( $\delta = 9.3$ ), methanol ( $\delta = 14.3$ ,  $\Delta\mu = 0.28$ ), acetone ( $\delta = 10.0$ ,  $\Delta\mu = 0.14$ ), and dioxane ( $\delta = 10.0$ ,  $\Delta\mu = 0.14$ ) / water ( $\delta = 23.4$ ,  $\Delta\mu$  is very high) (9/1, v/v).  $\delta$  means Hildebrand solubility parameter and  $\Delta\mu$  means the value of shift in wave length which is proportional to hydrogen bonding capacity. According to Schuerch, organic solvent which have Hildebrand solubility parameter around 11 and the value of shift in wave length of 0.14 or higher value have good solubility of lignin (Schuerch, 1952). However, these parameters are not exactly proportional to solubility of lignin exactly. Thus, according to the kind of lignin, appropriate fraction solvent can be varied.

**Table 1** Chemical and structural properties of lignin fractions

	Yield (%)	Mw (g/mol)	Mn (g/mol)	PDI (Mw/Mn)	Phe-OH (mmol/g)	Methoxyl (mmol/g)
MWL	-	8070	3670	2.2	1.6	4.2
F1	11.7	2410	1790	1.3	2.3	4.2
F2	11.7	2980	2310	1.3	2.2	4.0
F3	15.3	4320	2980	1.5	2.2	3.9
F4	11.8	4540	3200	1.4	2.1	3.8
F5	49.6	10640	5140	2.1	1.4	3.1
OL	-	4730	1680	2.8	1.1	5.6
F1	26.2	1470	1130	1.3	2.8	5.7
F2	26.1	2960	2010	1.5	1.6	6.1
F3	18.7	5470	2990	1.8	1.2	6.1
F4	3.7	7010	3810	1.8	1.0	4.9
F5	25.4	17090	9000	1.9	0.7	4.1
SL	-	3130	1030	3.0	1.8	3.4
F1	30.1	1190	660	1.8	2.6	3.9
F2	25.5	2550	1200	2.1	2.2	3.9
F3	24.7	3680	1630	2.3	1.7	3.5
F4	2.0	5310	2110	2.5	1.6	3.4
F5	11.2	14650	4700	3.1	0.8	3.1
INS	6.5	-	-	-	-	1.3

## 4.2. Molecular weight distributions of lignin fractions

The weight-average and number-average molecular weight and polydispersity index (PDI) of each fraction are shown in Table 1 and GPC curves are described in Fig. 4. Molecular weights of the original lignins were 8070 (MWL), 4730 (OL), and 3130 (SL). Molecular weights ( $M_w$ ) of the fractions increased from F1 (2410 for MWL, 1470 for OL, and 1190 for SL) to F5 (10640 for MWL, 10490 for OL, and 14650 for SL) with all lignins. This result indicates that lignin which has a relatively lower molecular weight (molecular size) has a higher solubility to organic solvents, while a higher molecular weight of lignin has a lower solubility. Polydispersity indexes (PDIs) of MWL fractions ranged from 1.3 to 2.1, while those for OL ranged from 1.3 to 1.9, and those for SL fractions ranged from 1.8 to 3.1. Earlier fractions having low molecular weights showed much lower PDI values than later fractions. However, all PDI values of lignin fractions were lower than the original lignins, which were 2.2 for MWL, 2.8 for OL, and 3.0 for SL. These results reveal that solvent fractionation could separate lignin macromolecules into specific molecular weight range and rendered lignin more homogenized. Similar results were reported in the study of successive solvent fractionation of kraft-AQ pulping lignin (Wang et al., 2010) and bamboo organosolv lignin (Li et al., 2012).



**Fig. 4.** GPC curves of (a) MWL, (b) OL, and (c) SL fractions

### 4.3. Determination of functional group contents

The phenolic hydroxyl groups are the most important functional group for lignin applications. The phenolic hydroxyl group content of lignins and their fractions was investigated by  $^1\text{H-NMR}$  as shown in Table 1. The content of hydroxyl groups decreased from F1 (2.3 mmol/g for MWL, 2.8 mmol/g for OL, and 2.6 mmol/g for SL) to F5 (1.4 mmol/g for MWL, 0.7 mmol/g for OL, and 0.8 mmol/g for SL), which indicates that the low molecular weight fractions had more phenolic hydroxyl groups. Thus, it is considered that a higher content of phenolic hydroxyl groups makes the lignin more soluble in solvent (Saito et al., 2014). Also, a high content of functional groups in lignin macromolecule suggests that the lower molecular weight lignins underwent more cleavage of internal linkages resulting in large amounts of end groups (Arshanitsa et al., 2013). A similar result was reported by Li. et al (Li et al., 2012).

The contents of methoxyl groups showed a similar trend to phenolic hydroxyl groups. As fractionation proceeded, the content of methoxyl groups generally decreased from F1 of MWL (4.2 mmol/g), OL (5.6 mmol/g), and SL (3.9 mmol/g) to F5 of them (3.1 mmol/g for MWL, 4.1 mmol/g for OL, and 3.1 mmol/g for SL) (Table 1). This decrease can be also explained as the smaller lignin macromolecules have more phenolic end groups which are not participating in any internal linkages.

Many previous studies have shown that functional groups in lignin play an important role in lignin applications (Duval & Lawoko, 2014) because they can determine some properties of lignin such as antioxidant ability (Gregorova et al., 2007; Li et al., 2012) or the number of reaction site (Argyropoulos et al., 2013; Dournel et al., 1988; Evtugin & Gandini, 1996; Li

& Ragauskas, 2012). As isolating the lignin fractions having different content of functional groups by solvent fractionation, it is expected that potential for utilization of lignin in these fields can be improved.

#### 4.4. Determination of S/G ratios of lignin fractions by DFRC

The yields of two monomers (G and S types) and S/G ratios of each lignin fraction obtained by DFRC are presented in Table 2. Monomers derived from the DFRC are usually derived from the cleavage of  $\beta$ -aryl-ether linkages. MWL (1062.9  $\mu\text{mol/g}$ ) yielded a much larger amount of DFRC monomers than OL (96.2  $\mu\text{mol/g}$ ) and SL (51.2  $\mu\text{mol/g}$ ). Aryl-ether linkages in MWL were preserved because MWL was extracted under a mild condition. However, OL and SL were extracted under relatively harsh conditions, thus, aryl-ether linkages in them were seemed to be cleaved during extraction which means they have more condensed structures. The S/G ratios of them were 2.1 for MWL, 1.5 for OL, and 0.7 for SL. Because MWL and OL were extracted from hardwood (yellow poplar), they had a higher amount of S units, while SL extracted from grasses showed the S/G ratio below 1.0.

Among lignin fractions, the sum of S/G monomers increased from F1 to F5 for all lignins. With MWL, the total amounts of DFRC monomers increased from 523.1  $\mu\text{mol/g}$  for F1 to 1220.2  $\mu\text{mol/g}$  for F5, while that with OL increased from 53.7  $\mu\text{mol/g}$  for F1 to 242.2  $\mu\text{mol/g}$  for F4. In SL, F1 yielded 31.9  $\mu\text{mol/g}$  of monomers while F5 yielded 73.3  $\mu\text{mol/g}$ . This results suggest that higher molecular weight fraction contains a larger amount of aryl-ether linkages, while lower molecular weight fractions have more condensed structures (Arshanitsa et al., 2013). Thus, DFRC monomers derived from cleavages of aryl-ether linkages increased as the molecular weight of the lignin fraction increased. As native OL and SL were considered to have fewer amounts of aryl-ether linkages than MWL, their fractions also contained fewer monomer than MWL fractions. However, there wasn't any noticeable trend for the S/G ratios between fractions.

**Table 2** Quantitative analysis of DFRC products of lignin fractions and their S/G ratios analyzed by DFRC

Sample	DFRC ( $\mu\text{mol/g}$ sample) <sup>a</sup>			S/G <sup>b</sup>
	G- CH=CHCH <sub>2</sub> OAc (Acetylated CA)	S- CH=CHCH <sub>2</sub> OAc (Acetylated SA)	total	
MWL	341.5 $\pm$ 18.7	721.4 $\pm$ 20.3	1062.9 $\pm$ 39.0	2.1
F1	196.0 $\pm$ 4.1	319.4 $\pm$ 11.4	515.4 $\pm$ 15.6	1.6
F2	333.0 $\pm$ 19.6	609.4 $\pm$ 25.0	942.4 $\pm$ 44.6	1.8
F3	327.4 $\pm$ 14.0	711.3 $\pm$ 30.2	1038.7 $\pm$ 44.2	2.2
F4	392.4 $\pm$ 17.0	803.8 $\pm$ 30.4	1196.2 $\pm$ 47.4	2.0
F5	372.3 $\pm$ 14.1	827.2 $\pm$ 31.4	1199.5 $\pm$ 45.6	2.2
OL	38.9 $\pm$ 4.0	57.3 $\pm$ 5.1	96.2 $\pm$ 9.1	1.5
F1	16.5 $\pm$ 2.3	37.2 $\pm$ 5.5	53.7 $\pm$ 9.8	2.3
F2	50.6 $\pm$ 0.2	93.6 $\pm$ 10.2	144.2 $\pm$ 10.4	1.8
F3	69.8 $\pm$ 7.1	143.3 $\pm$ 12.7	213.1 $\pm$ 19.8	2.1
F4	88.9 $\pm$ 6.4	153.3 $\pm$ 11.4	242.2 $\pm$ 17.8	1.7
F5	86.4 $\pm$ 5.3	151.4 $\pm$ 6.9	237.8 $\pm$ 12.2	1.8
SL	30.4 $\pm$ 2.2	20.8 $\pm$ 1.3	51.2 $\pm$ 3.5	0.7
F1	18.9 $\pm$ 0.4	13.0 $\pm$ 0.3	31.9 $\pm$ 0.7	0.7
F2	45.2 $\pm$ 1.1	9.9 $\pm$ 1.4	55.1 $\pm$ 2.5	0.2
F3	47.2 $\pm$ 4.2	18.0 $\pm$ 0.6	65.2 $\pm$ 4.8	0.4
F4	50.2 $\pm$ 1.9	15.6 $\pm$ 0.3	65.8 $\pm$ 2.2	0.3
F5	59.0 $\pm$ 2.3	14.3 $\pm$ 1.1	73.3 $\pm$ 3.4	0.2
INS	26.0 $\pm$ 6.7	1.2 $\pm$ 0.5	27.2 $\pm$ 7.2	0.0

<sup>a</sup> Data are means of duplicate analyses  $\pm$  S.D.

<sup>b</sup> Average molar ratios of sinapyl alcohol/coniferyl alcohol formed by the cleavage of  $\beta$ -O-4 linkages.

#### 4.5. Pyrolytic analysis of lignin fractions by Py-GC/MS

Py-GC/MS analysis was performed to investigate pyrolysis products and to determine H/G/S ratio of each fraction. The main 30 pyrolysis products are listed in table 3, 4, and 5, and the S/G ratio of each fraction is shown in table 6. The representative pyrolysis products of MWL fractions were syringol, 4-methylsyringol, syringaldehyde, and trans-isoeugenol. For OL, catechol, syringol, isoeugenol, 4-methylsyringol, 4-vinylsyringol, and 4-propenylsyringol were the main pyrolysis products. In SL, phenol, guaiacol, catechol, methylcatechol, and syringol were obtained mainly. The total amounts of pyrolysis products derived from MWL fractions ranged from 92.6 to 155.0 mmol/g, and those from OL fractions ranged from 56.8 to 106.6, while those from SL ranged between 49.6 and 77.6. Most of main products of MWL and OL were S unit compounds because both of them were derived from hardwood (yellow poplar); therefore, the S/G ratios of the lignins were higher than 1.0, which corresponded to the DFRC results. However, SL which was derived from non-woody biomass had relatively high amount of H units and the low S/G ratios. Interestingly, INS of SL showed very low yields of lignin-derived products and had some carbohydrate-derived products such as furan and pyran derivatives. This result indicates that SL INS contains not only lignin but also some carbohydrates which were not separated during soda pulping. This can explain why SL INS was not dissolved into lignin analysis solvents (THF and DMSO-d<sub>6</sub>). The S/G ratios of OL and their fractions ranged from 1.1 to 1.8 whereas those of MWL fractions ranged from 1.5 to 2.2. As SL had more H units and less S units than other lignins, S/G ratios of SL fractions were very low which ranged from 0.2 to 0.5.

The S/G ratio of each fraction showed such difference between the DFRC

and the Py-GC/MS results, especially for OL and SL fractions. The reason for these differences caused since the result of DFRC data is based on the release of only uncondensed monomers (Li & McDonald, 2014), while Py-GC/MS data was obtained by pyrolytic cleavage of lignin. Thus, these methods, especially DFRC, cannot give the precise S/G ratios. For this reason, OL and SL fractions, which had more condensed structures, showed bigger difference between two analyses results.

**Table 3** Pyrolysis products from lignin fractions of MWL using GC/MS analysis

Peak No.	Compounds	Yield (mg/g of lignin)					
		MWL	F1	F2	F3	F4	F5
1	Phenol	0.5	1.1	1.6	0.4	0.9	2.2
2	o-Cresol	0.6	0.7	0.6	0.5	1.0	0.9
3	p-Cresol	0.8	0.8	0.6	0.6	1.0	1.2
4	Guaiacol	1.6	2.2	2.9	2.8	1.9	1.4
5	Dimethylphenol	1.6	2.2	2.9	2.8	1.9	1.4
6	4-Methylguaiacol	2.4	4.0	3.2	4.8	1.4	3.2
7	Catechol	2.3	2.4	1.3	1.4	4.4	1.9
8	3-Methoxycatechol	3.6	3.1	2.6	3.5	3.9	2.7
9	3-Methylcatechol	2.9	2.7	1.9	1.9	4.3	2.1
10	4-Ethylguaiacol	0.6	1.1	0.7	0.9	0.5	0.6
11	4-Methylcatechol	0.2	1.1	1.5	0.6	1.8	2.0
12	4-Vinylguaiacol	1.2	1.6	1.7	2.0	1.3	1.6
13	Syringol	8.3	9.4	14.9	14.0	6.2	16.2
14	Eugenol	1.7	1.1	1.3	1.6	1.6	1.3
15	3,4-Dimethoxyphenol	2.0	1.5	1.1	1.7	0.8	1.3
16	Vanillin	1.1	1.1	0.9	1.2	1.7	1.0
17	cis-Isoeugenol	1.1	0.9	1.2	1.5	1.3	1.3
18	4-Methylsyringol	11.9	11.1	10.9	17.0	9.9	14.3
19	trans-Isoeugenol	7.6	5.9	8.8	11.9	6.1	9.4
20	Acetoguaiacone	0.6	0.5	0.6	0.7	0.6	0.5
21	4-Vinylsyringol	5.2	4.3	7.3	8.8	4.3	7.9
22	4-Allylsyringol	2.4	1.9	2.8	4.9	2.2	4.4
23	trans-4-Propenylsyringol	1.7	1.2	1.7	2.5	0.9	2.2
24	Syringaldehyde	18.5	13.5	17.8	27.3	15.7	25.1
25	trans-Coniferyl alcohol	0.3	0.0	0.4	0.6	0.4	0.3
26	Acetosyringone	6.8	4.8	6.7	10.3	5.6	9.0
27	Coniferaldehyde	3.3	2.4	4.2	5.4	3.5	5.0
28	Cis-coniferyl alcohol	3.3	2.4	4.2	5.4	3.5	5.0
29	Syringic acid	1.6	3.8	2.3	3.0	0.0	0.0
30	Sinapic aldehyde	5.5	1.2	5.4	10.4	4.4	0.0
	Sum (H-type)	2.7	3.8	3.6	2.8	4.6	5.5
	Sum (G-type)	30.6	30.2	37.2	47.1	35.0	38.5
	Sum (S-type)	68.8	62.7	76.5	105.0	53.0	84.7
	Total	102.2	96.7	117.3	155.0	92.6	128.7

**Table 4** Pyrolysis products from lignin fractions of OL using GC/MS analysis

Peak No.	Compounds	Yield (mg/g of lignin)					
		OL	F1	F2	F3	F4	F5
1	Phenol	0.6	0.5	0.6	0.7	0.3	0.6
2	o-Cresol	0.8	1.2	1.1	1.2	0.5	0.9
3	p-Cresol	0.7	0.6	0.8	1.1	0.5	1.0
4	Guaiacol	3.0	3.1	2.3	1.9	1.9	3.0
5	Dimethylphenol	0.9	1.4	1.6	1.6	0.5	1.1
6	4-Methylguaiacol	3.4	4.2	2.1	1.7	2.2	3.2
7	Catechol	3.9	6.0	4.0	5.3	2.4	2.4
8	3-Methoxycatechol	3.8	3.7	2.6	3.1	2.8	3.8
9	3-Methylcatechol	3.4	5.9	4.4	4.9	2.8	3.1
10	4-Ethylguaiacol	0.9	0.8	0.5	0.7	0.6	0.9
11	4-Methylcatechol	3.1	6.2	5.2	6.8	2.0	2.8
12	4-Vinylguaiacol	1.1	1.0	0.7	0.8	0.9	1.6
13	Syringol	13.0	10.2	9.2	7.7	8.7	13.6
14	Eugenol	2.4	3.5	2.8	3.6	1.9	2.8
15	3,4-Dimethoxyphenol	2.7	2.8	2.1	1.9	1.8	3.2
16	4-Ethylcatechol	0.8	1.7	0.8	2.0	0.0	0.0
17	Vanillin	0.9	1.9	0.8	0.5	0.8	0.8
18	4-Methylsyringol	9.3	8.4	5.1	5.6	6.6	9.4
19	Isoeugenol	5.7	3.9	3.0	3.3	5.5	8.5
20	Acetoguaiacone	0.4	0.3	0.2	0.2	0.4	0.5
21	4-Vinylsyringol	3.9	1.9	3.3	3.2	4.2	6.9
22	4-Allylsyringol	1.9	0.9	0.9	1.3	1.9	2.9
23	trans-4-Propenylsyringol	2.0	0.9	1.1	1.6	2.0	3.3
24	Syringaldehyde	8.8	9.5	4.6	4.4	9.2	11.5
25	cis-4-Propenylsyringol	6.6	2.9	3.2	4.4	7.3	9.9
26	Acetosyringone	4.9	1.8	2.0	3.0	5.0	7.1
27	Coniferaldehyde	1.3	0.0	0.3	1.1	1.7	2.8
28	Syringyl acetone	0.0	1.3	0.8	0.8	1.2	1.8
29	Propio-syringone	0.0	0.6	0.4	0.1	0.7	1.0
30	Sinapic aldehyde	0.5	0.0	0.0	0.0	2.0	2.7
	Sum (H-type)	3.4	4.2	4.9	5.4	1.8	4.0
	Sum (G-type)	31.5	39.1	23.7	26.6	25.6	38.0
	Sum (S-type)	50.9	41.7	28.2	30.3	45.0	64.6
	Total	85.0	85.0	56.8	62.2	72.4	106.6

**Table 5** Pyrolysis products from lignin fractions of SL using GC/MS analysis

Peak No.	Compounds	Yield (mg/g of lignin)						
		SL	F1	F2	F3	F4	F5	INS
1	Phenol	4.6	4.0	3.0	3.5	2.1	3.0	1.3
2	o-Cresol	2.2	2.5	1.6	1.9	1.3	1.7	0.6
3	p-Cresol	3.3	3.6	2.9	2.9	1.8	2.6	1.2
4	Guaiacol	4.5	2.5	3.1	2.6	3.0	2.1	0.8
5	2,4-Dimethylphenol	1.4	1.9	1.3	1.5	1.0	1.4	0.3
6	4-Ethylphenol	3.3	3.2	2.8	2.1	1.2	1.5	0.5
7	4-Methylguaiacol	3.7	2.8	4.2	2.5	3.4	2.0	1.5
8	Catechol	9.2	4.5	6.8	8.6	6.9	5.7	2.1
9	4-Vinylphenol	6.7	5.6	4.7	4.4	3.1	3.0	1.4
10	2-Ethyl-6-methylphenol	0.0	0.6	0.1	0.2	0.0	0.2	0.0
11	4-Ethyl-3-methylphenol	0.9	1.0	0.7	0.8	0.5	0.7	0.0
12	3-Methoxycatechol	2.7	1.4	2.5	1.7	2.5	0.8	0.2
13	3-Methylcatechol	4.5	4.7	4.1	3.9	4.3	3.5	0.0
14	4-Ethylguaiacol	2.3	1.8	2.5	1.2	1.4	0.9	0.3
15	4-Methylcatechol	7.6	7.6	6.3	7.4	5.2	6.4	0.0
16	4-Vinylguaiacol	4.5	3.8	4.1	3.0	3.2	1.9	1.1
17	4-Allylphenol	0.4	0.5	0.3	0.3	0.0	0.6	0.0
18	Syringol	6.0	3.0	4.3	3.2	4.9	1.9	0.8
19	Eugenol	2.2	2.1	2.1	1.7	2.8	1.6	0.0
20	3,4-Dimethoxyphenol	2.0	1.5	2.0	1.3	1.4	0.8	0.0
21	4-Ethylcatechol	2.8	2.0	2.4	2.0	1.6	1.7	0.0
22	Vanillin	0.6	0.4	0.5	0.0	0.6	0.0	0.2
23	4-Methylsyringol	2.7	1.9	3.3	1.8	3.7	1.1	0.5
24	Isoeugenol	3.8	2.9	4.2	2.7	5.5	2.5	1.3
25	Acetoguaiacone	0.5	0.3	0.3	0.2	0.3	0.1	0.0
26	2,6-Dimethyl-3-methoxymethyl-1,4-benzoquinone	1.0	0.6	1.0	0.7	1.2	0.4	0.3
27	trans-4-Propenylsyringol	0.4	0.3	0.5	0.2	0.8	0.2	0.0
28	Syringaldehyde	0.8	0.0	0.8	0.0	1.5	0.0	0.0
29	cis-4-Propenylsyringol	1.3	0.9	1.4	1.0	2.9	0.6	0.4
30	Acetosyringone	6.0	1.8	3.3	1.1	2.3	0.5	0.4
	Sum (H-type)	22.8	22.9	17.4	17.6	11.2	14.6	5.4
	Sum (G-type)	47.1	35.7	41.6	36.4	39.5	29.1	7.6
	Sum (S-type)	22.3	10.7	18.6	10.6	20.9	5.9	2.3
	Total	92.2	69.3	77.6	64.6	71.6	49.6	15.3

**Table 6** Comparison of S/G ratios determined by DFRC and Py-GC/MS analysis

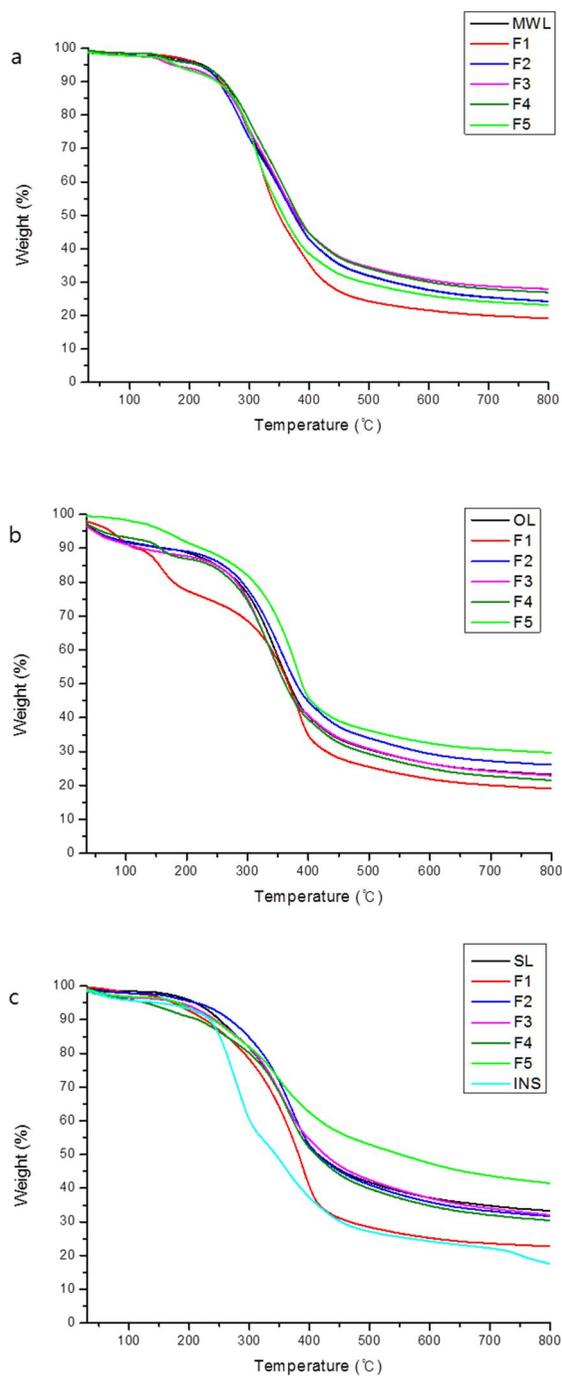
Lignin	S/G ratio		Lignin	S/G ratio		Lignin	S/G ratio	
	DFRC	Py-GC		DFRC	Py-GC		DFRC	Py-GC
MWL	2.1	2.2	OL	1.5	1.6	SL	0.7	0.5
F1	1.6	2.1	F1	2.3	1.1	F1	0.7	0.3
F2	1.8	2.1	F2	1.8	1.2	F2	0.2	0.4
F3	2.2	2.2	F3	2.1	1.1	F3	0.4	0.3
F4	2.0	1.5	F4	1.7	1.8	F4	0.3	0.5
F5	2.2	2.2	F5	1.8	1.7	F5	0.2	0.2
						INS	0.0	0.3

#### 4.6. Thermal decomposition characteristics of lignin fractions

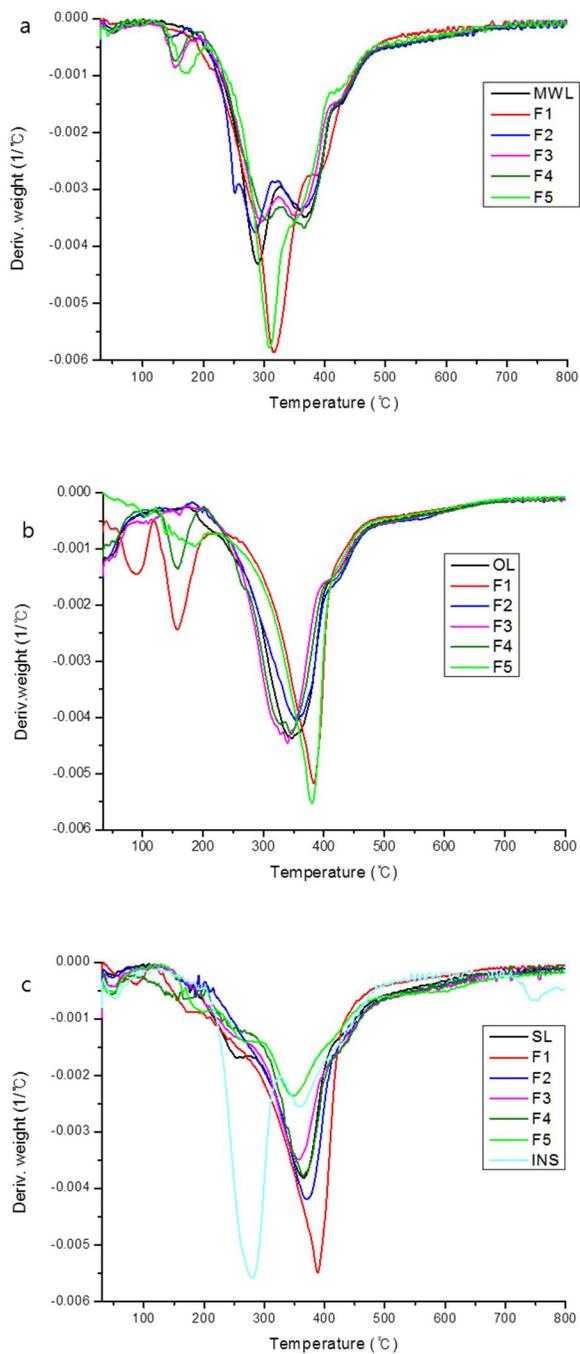
TGA was performed to investigate the thermal degradation properties of lignin fractions. TG thermograms are shown in Fig. 5 and amounts of char residue, maximum degradation temperature, and maximum degradation rate are shown in Table 7. With all lignins, F1 produced the smallest amounts of char residue (MWL F1: 21.8 %, OL F1: 28.8 %, and SL F1: 22.8 %), and these values tended to increase as the molecular weights of the fraction increased where F5 of MWL (27.9 %), OL (32.6 %), and SL (41.5 %) showed the highest char residue contents. The thermal degradation behavior of lignin is influenced by its molecular weight and functional groups, and thermal stability is proportional to the amount of char residue. According to previous studies, lignin with a higher molecular weight had higher thermal stability (Sun et al., 2000) and as the contents of functional groups like hydroxyl and methoxyl groups increased, the amount of char residues decreased (Jakab et al., 1997). Thus, earlier fractions with lower molecular weights and more functional groups yielded less char residue than later fractions due to their lower thermal stability compared to later fractions. In addition, as the temperature of degradation onset varied for each fraction, the temperature for lignin-polymer blending should differ, which is lower than the degradation onset temperature (Mousavioun & Doherty, 2010).

DTG graphs are shown in Fig. 6 and the maximum degradation temperature and rate are shown in Table 7. While thermal degradation of lignin occurs generally from 100 °C to 800 °C, there are the number of major thermal degradation regions in the temperature ranges of 130 ~ 200 °C, 200 ~ 270 °C, 300 ~ 400 °C, and up to 400 °C (Sahoo et al., 2011). All three lignin fractions showed somewhat different tendencies of thermal degradation.

It was reported that  $\alpha$ - and  $\beta$ -aryl-alkyl-ether linkages cleave between 150 °C and 300 °C (Balat, 2008); thus, later fractions that contain more  $\alpha$ - and  $\beta$ -aryl-alkyl-ether linkages showed tendencies to be degraded around 300 °C. It was also reported that methyl-aryl ether bond cleavage occurs mainly between 300 and 400 °C (Jakab et al., 1997; Tejado et al., 2007) and carbon-carbon linkages cleave at temperatures of 370 ~ 400 °C. In the DTG curves, earlier fractions, especially F1, generally degraded near 370 °C, and this tendency was considered to reflect the main thermal cleavage of earlier fractions being cleavage of carbon-carbon bonds between lignin molecules. With MWL, F2, F3, and F4 showed similar degradation behaviors that indicated they had similar thermal properties. In contrast, the maximum degradation temperatures and rates of F1 and F5 were relatively higher than those of the others, indicating that their thermal properties were distinct from those of others. However, average maximum degradation temperature of MWL fractions ranged around 300 °C, which were relatively lower than other lignin fractions. As discussed above, MWL and its fractions have more aryl ether linkages than other lignin fractions, thus this difference seemed to cause the relatively lower maximum degradation temperature of MWL fractions. In case of SL, maximum degradation temperature and rate of fractions decreased gradually from F1 to F5. Interestingly, SL INS showed much different degradation behavior which remained the lowest char residue and maximum degradation temperature. This can be explained by the fact that INS contains not only lignin but also some carbohydrate. It has been reported that hemicellulose degraded mainly around 260 °C thus SL INS is supposed to be composed of complex of lignin and hemicellulose. It also makes sense with the results of Py-GC/MS which revealed that SL INS contains some carbohydrates.



**Fig. 5.** TG thermograms of lignin fractions: (a) MWL, (b) OL, and (c) SL



**Fig. 6** DTG thermograms of lignin fractions: (a) MWL, (b) OL, and (c) SL

**Table 7** The yield of char residue, maximum degradation temperature, and maximum degradation rate of lignin fractions obtained from TG/DTG analysis

	Char (%)	Max. degradation temp. (°C)	Max. degradation rate (1/°C)
MWL	25.6	300	0.0043
F1	21.8	316	0.0059
F2	24.3	285	0.0038
F3	27.9	297	0.0036
F4	27.6	282	0.0037
F5	29.3	309	0.0058
OL	23.2	353	0.0044
F1	28.8	375	0.0052
F2	30.3	365	0.0041
F3	33.1	340	0.0045
F4	32.0	355	0.0043
F5	32.6	342	0.0055
SL	33.3	363	0.0038
F1	22.8	388	0.0055
F2	31.7	368	0.0042
F3	32.0	355	0.0035
F4	30.5	364	0.0038
F5	41.5	347	0.0024
INS	17.5	279	0.0056

## 4.7. Analyses of lignin-grafted-PLLA copolymers

### 4.7.1. Features of grafted PLLA onto lignin

L-lactide was grafted onto hydroxyl groups in lignin and the conversion ratios of L-lactide to lignin-g-PLLA were calculated by  $^1\text{H}$  NMR. The resonances at 5.2 ~ 5.1 are assigned to the protons of the lignin-g-PLLA repeating unit ( $\text{H}_a$ ), while those at 5.05 represent the protons of the non-converted L-lactide ( $\text{H}_b$ ) (Chung et al., 2013; Zong et al., 2016). Thus, the conversion ratio of L-lactide to lignin-g-PLLA can be calculated through the following formula;

$$\text{Conversion ratio (\%)} = \frac{\text{H}_a}{\text{H}_a + \text{H}_b} \times 100$$

Calculated conversion ratios were given in table 8. Because of insolubility of SL INS into NMR solvent, conversion ratio of SLINS-g-PLLA was not able to be determined. Averagely, about 90 % of L-lactide was converted into lignin-g-PLLA. Among them, PLLA grafted onto SL F1 showed the highest conversion ratio (91.2 %) while SL F5 had the lowest ratio (88.3 %). This result was attributed to the difference of content of hydroxyl groups in each lignin fraction. When L-lactide formed poly(L-lactide) chain via ring-opening polymerization onto lignin macromolecule, it is grafted onto hydroxyl groups in lignin (Chung et al., 2013). Thus, F1 which has relatively more hydroxyl groups can give L-lactide more opportunity to be grafted onto hydroxyl groups. In contrast, F5 contains fewer amount of hydroxyl group, which lead L-lactide to get fewer chances to meet hydroxyl groups.

The molecular weight of PLA which corresponds to its chain length plays an important role in its properties. Thus, GPC analysis was performed to investigate the number-average molecular weight ( $M_n$ ) of each grafted PLLA. The results of GPC were given in table 8. The molecular weights of lignin-g-PLLA were increased from 840 for SLF1-g-PLLA to 16140 for SLF5-g-PLLA. The ratio of lignin and L-lactide were fixed in all fractions, thus, as SL F1 has more hydroxyl groups which act as initiation site of PLLA grafting, the number of PLLA chains formed on SL F1 could be also larger, which means the chain length of PLLA could be shorter than other fractions. By contrast, in case of SL F5, it has less initiation site thus it could lengthen its PLLA chain length.

**Table 8** Conversion ratios of lignin-g-PLLA

Copolymer	Conversion ratio (%)	Molecular weight ( $M_n$ )
SL-g-PLLA	90.8	880
SLF1-g-PLLA	91.2	840
SLF3-g-PLLA	89.7	8890
SLF5-g-PLLA	88.3	16140
SLINS-g-PLLA	N.D	N.D

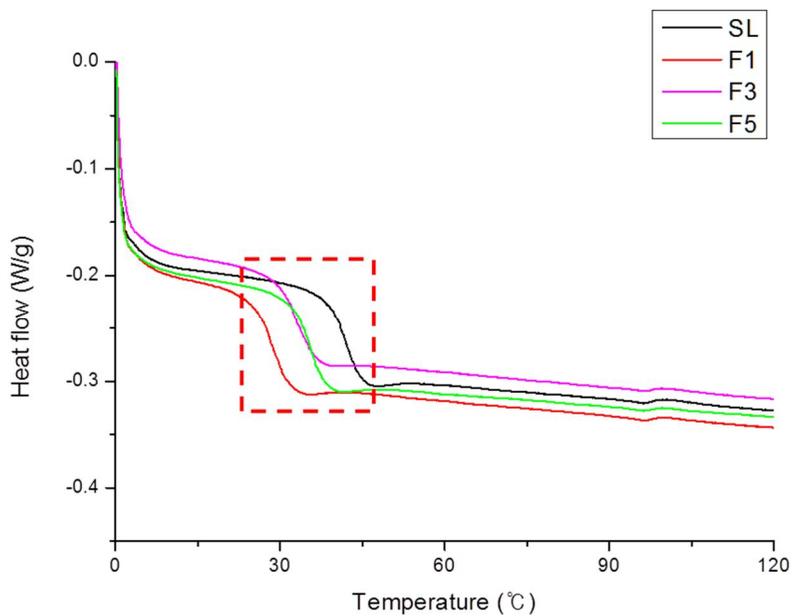
**N.D: Not determined**

#### **4.7.2. Thermal properties of lignin-g-PLLA**

DSC analysis was performed to determine the glass transition temperature ( $T_g$ ) of copolymers and the results were given in Table 9 and DSC curves were shown in Fig. 7. As molecular weight of lignin fraction increased, the  $T_g$  of lignin-PLLA copolymer seemed to be increased from 28.2 for SLF1-g-PLLA to 35.2 for SLF5-g-PLLA. This can be explained by the fact that high molecular weight lignin has relatively higher  $T_g$  than low molecular weight lignin (Gregorova, 2013), and they also formed longer PLLA chain which also contributed to increase of  $T_g$ . However,  $T_g$  of copolymer grafted with lignin fractions were lower than that of copolymer grafted with native SL as SL has the most complex and heterogeneous structures which might enhance its  $T_g$ .

**Table 9** Glass transition temperatures of lignin-g-PLLAs determined by DSC

Sample	Glass transition temperature (°C)
SL-g-PLLA	41.7
SLF1-g-PLLA	28.2
SLF3-g-PLLA	33.0
SLF5-g-PLLA	35.2
SLINS-g-PLLA	-
<b>N.D: Not determined</b>	

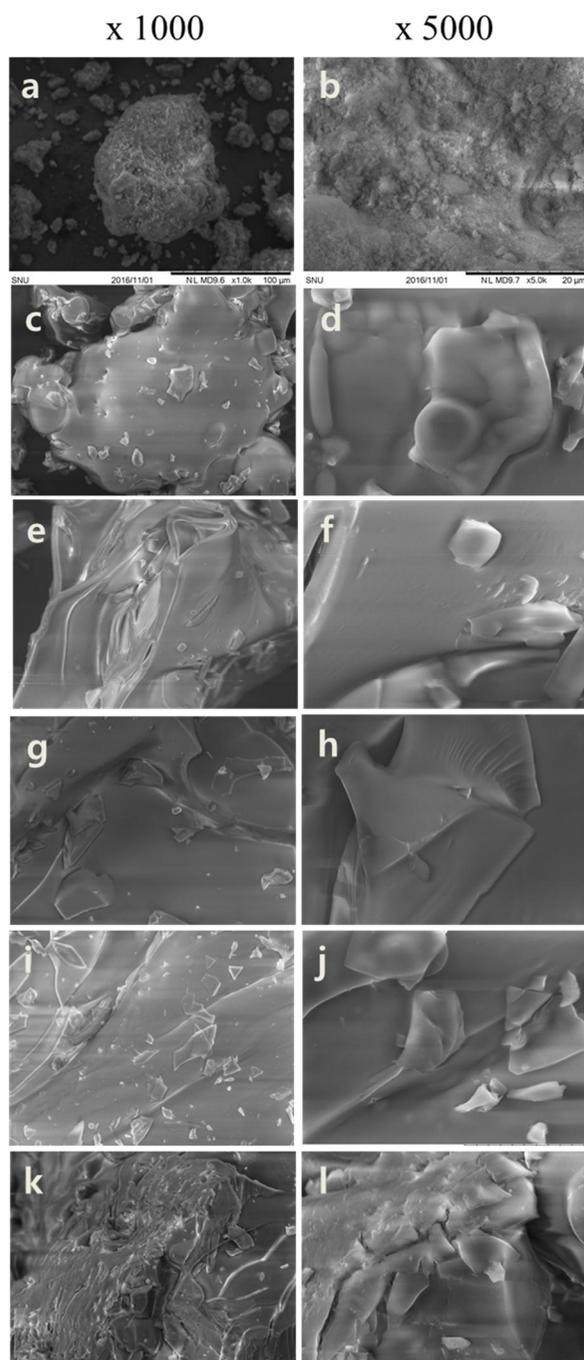


**Fig. 7.** DSC curves of lignin-g-PLLA. Red-dotted square indicates the glass transition temperature area

### 4.7.3. Surface characterization of lignin-g-PLLA

Surface of SL fractions grafted with PLLA were investigated by SEM (Fig. 8). According to SEM images, original SL has rough and irregular face as shown in Fig. 8. a and b. In contrast, SL grafted with PLLA (Fig. 8. c, d) showed smoother surface than original indicating that PLLA coated the surface of SL but rougher than those of fractions. SL F1, F3 and F5 (Fig. 8. e-j) showed more smooth surface compared to SL and SL INS which reveals that they grafted with PLLA successful. Among them, F1 seemed to have the smoothest surface. As discussed above, SL F1 has more hydroxyl groups than other fractions, thus it is supposed that its surface was coated with PLLA more uniformly which lead it to have relatively smoother surface. In case of SLINS-g-PLLA (Fig. 8. k,l), it seemed to have rough and rocky surface meaning that grafting of PLLA onto SL INS was unsatisfactory.

Surface property of lignin-g-PLLA plays very important role when it forms a composite. When filler is blended with a polymer, interface between two materials has a huge effect on its mechanical properties. If there is not enough interaction between their surfaces, mechanical properties of that composite must be worsen. Thus, it is important to consider the interfacial interaction between two materials. As grafting of PLLA onto lignin surface, the interfacial interaction between lignin and PLA can be enhanced, thus mechanical properties of the composite are expected to be kept or increased (Chung et al., 2013). Therefore, it is expected that PLA composites of SL F1, F3, and F5 which were relatively uniformly coated show better mechanical properties than composites of SL and INS.



**Fig. 8.** SEM images of SL and their fractions grafted with PLLA. (a, b) original SL, (c, d) SL-g-PLLA, (e, f) SLF1-g-PLLA, (g, h) SLF3-g-PLLA, (i, j) SLF5-g-PLLA, and (k, l) SLINS-g-PLLA.

#### **4.7.4. Mechanical properties of lignin-g-PLLA composites**

Early studies that blended lignin with PLA had the decreased tensile properties because simple blending causes inconsistency on the interfacial interaction. As unmodified lignin cannot interact with PLA strongly due to their low superficial affinity, lignin blended PLA showed severe decline of mechanical properties even if thermal or optical properties were enhanced (Chung et al., 2013; Li et al., 2003). However, as the method of grafting PLLA onto lignin emerged recently, lignin-grafted-PLA composites have been able to be produced without significant reduction of mechanical properties.

Tensile test was conducted to investigate effect of lignin-g-PLLA on PLA mechanical properties and the results were given in Table 10. Tensile strength and modulus were determined and shown in table 10. PLA/SLF3-g-PLLA showed the highest tensile strength (68.5 MPa) compared to pure PLA (66.1 MPa) and other PLA/lignin-g-PLLA ranged from 60 to 64 MPa. In PLA composite, both molecular weight and interfacial interaction are the important factors to determine mechanical properties of composites. Previous studies revealed that mechanical properties of PLA increase as chain length of PLA increase (Pillin et al., 2008; Yoon et al., 2010), and the importance of interfacial interaction was already discussed in 4.7.3. SLF3-g-PLLA showed relatively higher molecular weight of 8890 than SL or F1 and it also had well-coated surface according to SEM images. SL copolymer was expected to have weaker interfacial interaction with PLA due to roughness and heterogeneity of its surface, and actually showed lower tensile strength. Although F1 had the smoothest surface among copolymers, the chain length of F1 copolymer is considered to be too short to improve the tensile strength of PLA. On the other hand, F5 copolymers which had the longest chain length also showed

lower tensile strength, and it seemed that because F5 had larger and heterogeneous molecular, it couldn't contribute to enhance the tensile strength of PLA. In case of INS, INS copolymer which had relatively rough and irregular surface property showed much lower tensile strength (45.0 MPa) than other fraction copolymers and even native SL copolymer due to its poor interfacial interaction with PLA.

Tensile modulus (Young's modulus) was also determined. In case of tensile modulus, PLA/SLF5-g-PLLA showed the highest value of 2503.4 MPa, even higher than pure PLA. Longest PLLA chain on the SLF5-g-PLLA seemed to contribute to its increased modulus which agree the results of previous studies (Cohn & Salomon, 2005; Yoon et al., 2010). According to Chung et al., appropriate grafted PLA chain length can have a synergistic reinforcement effect on the tensile modulus of PLA (Chung et al., 2013). On the other hand, F1 copolymer showed the lowest elastic modulus of 2197.7 MPa due to its chain length which was too short to reinforce the tensile modulus.

It has been revealed that lignin grafted with PLLA can improve the mechanical properties of PLA materials and in this study, it was proven that each fractionated lignin grafted with PLLA having different chain lengths and surface characters affect differently on the tensile strength of lignin-PLA composites. However, it can be also varied by change of some factors. The chain length of lignin-g-PLLA can be controlled by the ratio of lignin and L-lactide, and properties of PLA/lignin-g-PLLA might also vary according to the concentration of lignin copolymer in the PLA. Thus, various PLA/lignin-g-PLLA composites having different concentration should be investigated to identify the effect of lignin concentration on the mechanical properties of PLA. In addition, it was supposed that other properties of PLA such as optical

properties or thermal properties might be influenced by the different properties of lignin fractions. Therefore, further study must be needed to investigate the effect of lignin-g-PLLA on the various properties of PLA materials.

**Table 10** Tensile strength and modulus of lignin-g-PLLA

Sample	Tensile strength (MPa)	Tensile modulus (MPa)
PLA <sup>a</sup>	66.1 ( $\pm$ 2.1)	2442.4 ( $\pm$ 183.5)
SL <sup>b</sup>	60.3 ( $\pm$ 2.9)	2324.4 ( $\pm$ 240.3)
F1 <sup>b</sup>	63.9 ( $\pm$ 2.8)	2197.7 ( $\pm$ 140.0)
F3 <sup>b</sup>	68.5 ( $\pm$ 2.3)	2422.6 ( $\pm$ 106.2)
F5 <sup>b</sup>	63.5 ( $\pm$ 1.5)	2503.4 ( $\pm$ 175.2)
INS <sup>b</sup>	52.0 ( $\pm$ 5.4)	2229.6 ( $\pm$ 216.9)

<sup>a</sup> Sample prepared with PLA 2002D

<sup>b</sup> Sample prepared with mixture of corresponding lignin-g-PLLA and PLA 2002D in a ratio of 1:20

## 5. Conclusion

Three lignins (MWL, OL, and SL) were sequentially fractionated with five kinds of organic solvents which were ethyl acetate, 2-butanone, methanol, acetone, and dioxane/water (95:5 v/v) in order of increasing solubility of lignin. The yields of lignin fractions were varied since each lignin has different solubility to solvents. Molecular weight of lignin increased from F1 to F5, and their PDI values were lower than native lignin indicating that solvent fractionation can help; lignin being homogeneous. Functional group contents of lignin fractions decreased as molecular weights of fractions increased. The yields of DFRC monomers were higher in later fractions resulted from the fact that they have more aryl-ether linkages. S/G ratios were determined by both DFRC and Py-GC/MS but ratios between them showed some differences since only uncondensed monomer might be analyzed by DFRC. Thermogravimetric analysis revealed that F1 had the lowest thermal stability and thermal degradation behaviors of lignin fractions varied due to their structural differences.

To investigate the potential of lignin fractions for utilization as lignin-PLA composites, SL and its fractions were grafted with L-lactide via ring-opening polymerization. F1-g-PLLA showed the highest conversion ratio since it had the largest amount of hydroxyl groups where L-lactide might be grafted. However, F1-g-PLLA seemed to have the lowest molecular weight while F5-g-PLLA had the highest. DSC analysis revealed that F1-g-PLLA had the lowest glass transition temperature and SL-g-PLLA had the highest. SEM images suggested that as PLLA grafted onto surface of lignin, its surface became smooth which might enhance the interfacial interaction with PLA.

Especially, SL F1, F3, and F5 copolymers had smoother surfaces than those of SL and SL INS. The results of tensile strength were varied by chain lengths and interfacial interactions of copolymers. In case of tensile modulus, the chain length of copolymer affected mainly. As these mechanical properties can be changed by control of lignin/PLA ratios, further study is needed to be performed to investigate the effect of different lignin concentration on PLA properties. In addition, other properties such as thermal and optical properties should also be investigated.

## 6. References

- Achyuthan, K.E., Achyuthan, A.M., Adams, P.D., Dirk, S.M., Harper, J.C., Simmons, B.A., Singh, A.K. 2010. Supramolecular self-assembled chaos: polyphenolic lignin's barrier to cost-effective lignocellulosic biofuels. *Molecules*, **15**(12), 8641-8688.
- Argyropoulos, D.S., Sadeghifar, H., Cui, C., Sen, S. 2013. Synthesis and characterization of poly (arylene ether sulfone) kraft lignin heat stable copolymers. *ACS Sustainable Chemistry & Engineering*, **2**(2), 264-271.
- Arshanitsa, A., Ponomarenko, J., Dizhbite, T., Andersone, A., Gosselink, R.J., van der Putten, J., Lauberts, M., Telysheva, G. 2013. Fractionation of technical lignins as a tool for improvement of their antioxidant properties. *Journal of Analytical and Applied Pyrolysis*, **103**, 78-85.
- Baker, F. 2010. Low cost carbon fiber from renewable resources. *EERE, US Dept of Energy Project ID# Im\_03\_baker*.
- Baker, S. 1996. Rapid methoxyl analysis of lignins using gas chromatography. *Holzforschung*, **50**(6), 573-574.
- Balat, M. 2008. Mechanisms of thermochemical biomass conversion processes. Part 1: reactions of pyrolysis. *Energy Sources, Part A*, **30**(7), 620-635.
- Björkman, A. 1956. Studies on finely divided wood. Part 1. Extraction of lignin with neutral solvents. *Svensk papperstidning*, **59**(13), 477-485.
- Chung, Y.-L., Olsson, J.V., Li, R.J., Frank, C.W., Waymouth, R.M., Billington, S.L., Sattely, E.S. 2013. A renewable lignin–lactide copolymer and application in biobased composites. *ACS Sustainable Chemistry & Engineering*, **1**(10), 1231-1238.
- Cohn, D., Salomon, A.H. 2005. Designing biodegradable multiblock PCL/PLA thermoplastic elastomers. *Biomaterials*, **26**(15), 2297-2305.
- Dournel, P., Randrianalimanana, E., Deffieux, A., Fontanille, M. 1988.

- Synthesis and polymerization of lignin macromonomers—I. Anchoring of polymerizable groups on lignin model compounds. *European polymer journal*, **24**(9), 843-847.
- Duval, A., Lawoko, M. 2014. A review on lignin-based polymeric, micro-and nano-structured materials. *Reactive and Functional Polymers*, **85**, 78-96.
- Evtugin, D., Gandini, A. 1996. Polyesters based on oxygen-organosolv lignin. *Acta polymerica*, **47**(8), 344-350.
- Evtugin, D., Andreolety, J., Gandini, A. 1998. Polyurethanes based on oxygen-organosolv lignin. *European polymer journal*, **34**(8), 1163-1169.
- Gosselink, R.J., van Dam, J.E., de Jong, E., Scott, E.L., Sanders, J.P., Li, J., Gellerstedt, G. 2010. Fractionation, analysis, and PCA modeling of properties of four technical lignins for prediction of their application potential in binders. *Holzforschung*, **64**(2), 193-200.
- Gregorová, A., Cibulková, Z., Košíková, B., Šimon, P. 2005. Stabilization effect of lignin in polypropylene and recycled polypropylene. *Polymer Degradation and Stability*, **89**(3), 553-558.
- Gregorova, A. 2013. *Application of differential scanning calorimetry to the characterization of biopolymers*. INTECH Open Access Publisher.
- Gregorova, A., Košíková, B., Staško, A. 2007. Radical scavenging capacity of lignin and its effect on processing stabilization of virgin and recycled polypropylene. *Journal of applied polymer science*, **106**(3), 1626-1631.
- Hewson, W.B., McCarthy, J.L., Hibbert, H. 1941. Studies on Lignin and Related compounds. LVII. Mechanism of the Ethanolysis Reaction. *Journal of the American Chemical Society*, **63**(11), 3041-3045.
- Jakab, E., Faix, O., Till, F. 1997. Thermal decomposition of milled wood lignins studied by thermogravimetry/mass spectrometry. *Journal of Analytical and Applied Pyrolysis*, **40**, 171-186.
- Kadla, J., Kubo, S., Venditti, R., Gilbert, R., Compere, A., Griffith, W. 2002.

- Lignin-based carbon fibers for composite fiber applications. *Carbon*, **40**(15), 2913-2920.
- Kelley, S.S., Ward, T.C., Rials, T.G., Glasser, W.G. 1989. Engineering plastics from lignin. XVII. Effect of molecular weight on polyurethane film properties. *Journal of applied polymer science*, **37**(10), 2961-2971.
- Kirk, T., Brown, W., Cowling, E. 1969. Preparative fractionation of lignin by gel-permeation chromatography. *Biopolymers*, **7**(2), 135-153.
- Laurichesse, S., Avérous, L. 2013. Synthesis, thermal properties, rheological and mechanical behaviors of lignins-grafted-poly ( $\epsilon$ -caprolactone). *Polymer*, **54**(15), 3882-3890.
- Li, H., McDonald, A.G. 2014. Fractionation and characterization of industrial lignins. *Industrial Crops and Products*, **62**, 67-76.
- Li, J., He, Y., Inoue, Y. 2003. Thermal and mechanical properties of biodegradable blends of poly (L-lactic acid) and lignin. *Polymer International*, **52**(6), 949-955.
- Li, M.-F., Sun, S.-N., Xu, F., Sun, R.-C. 2012. Sequential solvent fractionation of heterogeneous bamboo organosolv lignin for value-added application. *Separation and Purification Technology*, **101**, 18-25.
- Li, Y., Ragauskas, A.J. 2012. Kraft lignin-based rigid polyurethane foam. *Journal of Wood Chemistry and Technology*, **32**(3), 210-224.
- Mörck, R., Yoshida, H., Kringstad, K.P., Hatakeyama, H. 1986. Fractionation of kraft lignin by successive extraction with organic solvents. 1. Functional groups (13) C-NMR-spectra and molecular weight distributions. *Holzforschung (Germany, FR)*.
- Mousavioun, P., Doherty, W.O. 2010. Chemical and thermal properties of fractionated bagasse soda lignin. *Industrial Crops and Products*, **31**(1), 52-58.
- Pandey, M.P., Kim, C.S. 2011. Lignin depolymerization and conversion: a review of thermochemical methods. *Chemical Engineering & Technology*, **34**(1), 29-41.
- Pillin, I., Montrelay, N., Bourmaud, A., Grohens, Y. 2008. Effect of thermo-

- mechanical cycles on the physico-chemical properties of poly (lactic acid). *Polymer Degradation and Stability*, **93**(2), 321-328.
- Ragauskas, A.J., Williams, C.K., Davison, B.H., Britovsek, G., Cairney, J., Eckert, C.A., Frederick, W.J., Hallett, J.P., Leak, D.J., Liotta, C.L. 2006. The path forward for biofuels and biomaterials. *science*, **311**(5760), 484-489.
- Sahoo, S., Seydibeyoğlu, M., Mohanty, A., Misra, M. 2011. Characterization of industrial lignins for their utilization in future value added applications. *Biomass and bioenergy*, **35**(10), 4230-4237.
- Saito, T., Perkins, J.H., Vautard, F., Meyer, H.M., Messman, J.M., Tolnai, B., Naskar, A.K. 2014. Methanol fractionation of softwood kraft lignin: impact on the lignin properties. *ChemSusChem*, **7**(1), 221-228.
- Schuerch, C. 1952. The solvent properties of liquids and their relation to the solubility, swelling, isolation and fractionation of lignin. *Journal of the American Chemical Society*, **74**(20), 5061-5067.
- Sun, R., Tomkinson, J., Jones, G.L. 2000. Fractional characterization of ash-AQ lignin by successive extraction with organic solvents from oil palm EFB fibre. *Polymer Degradation and Stability*, **68**(1), 111-119.
- Tejado, A., Pena, C., Labidi, J., Echeverria, J., Mondragon, I. 2007. Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis. *Bioresource Technology*, **98**(8), 1655-1663.
- Thring, R., Vanderlaan, M., Griffin, S. 1996. Fractionation of Alcell® lignin by sequential solvent extraction.
- Toledano, A., García, A., Mondragon, I., Labidi, J. 2010. Lignin separation and fractionation by ultrafiltration. *Separation and Purification Technology*, **71**(1), 38-43.
- Vanderlaan, M., Thring, R. 1998. Polyurethanes from Alcell® lignin fractions obtained by sequential solvent extraction. *Biomass and bioenergy*, **14**(5), 525-531.
- Wallberg, O., Jönsson, A.-S., Wimmerstedt, R. 2003. Fractionation and

- concentration of kraft black liquor lignin with ultrafiltration. *Desalination*, **154**(2), 187-199.
- Wang, K., Xu, F., Sun, R. 2010. Molecular characteristics of kraft-AQ pulping lignin fractionated by sequential organic solvent extraction. *International journal of molecular sciences*, **11**(8), 2988-3001.
- Yaku, F., Tanaka, R., Koshijima, T. 1981. Lignin Carbohydrate Complex. Pt. IV. Lignin as Side Chain of the Carbohydrate in Björkman LCC. *Holzforschung-International Journal of the Biology, Chemistry, Physics and Technology of Wood*, **35**(4), 177-181.
- Yoon, J.T., Lee, S.C., Jeong, Y.G. 2010. Effects of grafted chain length on mechanical and electrical properties of nanocomposites containing polylactide-grafted carbon nanotubes. *Composites Science and Technology*, **70**(5), 776-782.
- Yoshida, H., Mörck, R., Kringstad, K.P., Hatakeyama, H. 1987. Fractionation of kraft lignin by successive extraction with organic solvents. II. Thermal properties of kraft lignin fractions. *Holzforschung-International Journal of the Biology, Chemistry, Physics and Technology of Wood*, **41**(3), 171-176.
- Yue, X., Chen, F., Zhou, X., He, G. 2012. Preparation and characterization of poly (vinyl chloride) polyblends with fractionated lignin. *International Journal of Polymeric Materials*, **61**(3), 214-228.
- Zhang, X., Tu, M., Paice, M.G. 2011. Routes to potential bioproducts from lignocellulosic biomass lignin and hemicelluloses. *BioEnergy Research*, **4**(4), 246-257.
- Zong, E., Liu, X., Fu, S., Xu, Y., Chu, F. 2016. Combination of lignin and l-lactide towards grafted copolymers from lignocellulosic butanol residue. *International journal of biological macromolecules*.

# 초 록

본 연구에서는 milled wood lignin (MWL), organosolv lignin (OL), soda lignin (SL) 3 종류의 리그닌을 ethyl acetate (F1), 2-butanone (F2), methanol (F3), acetone (F4), dioxane/water (95:5 v/v, F5) 5 가지의 유기용매를 이용하여 순차적으로 분획하였다. 각 리그닌 별 분획물의 수율은 MWL의 경우 11.7%, 11.7%, 15.3%, 11.8%, 49.6% 였고, OL의 경우 26.2%, 26.1%, 18.7%, 3.7%, 25.4% 였으며, SL은 30.1%, 25.5%, 24.7%, 2.0%, 11.2%의 수율과 6.5%의 insoluble fraction (INS)을 나타내었다. GPC를 이용한 분자량 측정 결과 모든 리그닌에서 F1의 분자량이 1000에서 2400 Da. 사이로 가장 낮았으며 F5의 분자량은 10000 이상으로, F1에서 F5로 갈수록 분자량이 증가하는 경향을 보였다. 각 분획물의 작용기 함량 측정 결과 분획물의 분자량이 증가함에 따라 페놀 수산기와 메톡실기의 함량이 감소하는 것으로 나타났다. DFRC 분석 결과 분자량이 높은 분획물이 더 많은 DFRC 모노머 수율을 나타내었으며, 이는 분자량이 높을수록 리그닌이 더 많은 aryl-ether 결합을 함유하고 있음을 의미한다. Py-GC/MS 분석을 통해서 각각의 리그닌 분획물의 열분해 산물에 대한 분석이 이루어졌으며 DFRC와 Py-GC/MS 분석을 통한 S/G ratio 비교 결과 리그닌 구조의 축합 정도에 따라서 두 분석간의 차이가 존재함을 확인하였다. 열중량분석(TGA) 결과 분자량이 낮은 리그닌 분획이 더 낮은 열적 안정성을 보였으며, 이는 이들이 더 많은 작용기를 함유하고 있기 때문인 것으로 사료된다.

분획된 리그닌의 활용 가능성 탐색을 위하여 SL과 그 분획물들이 각각 L-lactide와 개환반응(ring-opening

polymerization)을 통해서 공중합되었다. 각각의 분획물에서 L-lactide가 PLLA로 전환된 비율을 측정한 결과 수산기를 가장 많이 함유하고 있는 F1에서 전환율이 91.2%로 가장 높은 것으로 나타났으며 반대로 수산기를 가장 적게 가지는 F5에서 그 비율이 88.3%로 가장 낮았다. 하지만 분자량 측정 결과 F5 공중합체가 가장 분자량이 높은 것으로 조사되었으며 따라서 F5 공중합체가 가장 긴 PLLA 사슬을 가지는 것으로 보인다. 시차주사열량계(DSC)를 통한 유리전이온도( $T_g$ ) 측정 결과 분자량이 가장 낮은 F1 공중합체가 가장 낮은 유리전이온도를 나타내었으며 그 구조가 비교적 복잡하고 불규칙한 SL 공중합체가 가장 높은 유리전이온도를 나타내었다. 주사전자현미경(SEM)을 이용하여 공중합체의 표면 분석을 통해서 리그닌 표면에 PLLA가 공중합됨에 따라 리그닌 표면이 더 매끈해지는 현상이 관찰되었으며, F1, F3, F5가 더 매끈한 표면을 가지는 것을 확인하였다. 각각의 공중합체를 PLA 2002D와 혼합하여 리그닌-PLA 복합체를 제조하였으며, 이에 대한 인장강도(tensile strength)와 인장탄성계수(tensile modulus)를 측정하였다. 인장강도의 경우 공중합체의 PLLA 사슬 길이와 표면 특성에 모두 영향을 받는 반면, 모듈러스(tensile modulus)는 사슬 길이에 주로 영향을 받는 것으로 나타났다.