2017

Biorefinery lignin as filler material in polylactic acid composite

Yiwei Gao
Iowa State University

Recommended Citation

Gao, Yiwei, "Biorefinery lignin as filler material in polylactic acid composite" (2017). *Graduate Theses and Dissertations*. 16133.
https://lib.dr.iastate.edu/etd/16133

Biorefinery lignin as filler material in polylactic acid composite

by

Yiwei Gao

A thesis submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Mechanical Engineering

Program of Study Committee:
Xianglan Bai, Major Professor
Xinwei Wang
Eric W. Cochran

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2017

TABLE OF CONTENTS

LIST OF FIGURES

Page

LIST OF TABLES

NOMENCLATURE

TGA	Thermogravimetric Analysis
FTIR	Fourier Transform Infrared Spectroscopy
ICP MS	Inductively coupled plasma mass spectrometry
MPT	Mechanical Property Test
DSC	Differential Scanning Calorimetry
DHR	Discover Hybrid Rheometer
HL	Hardwood Lignin
SL	Softwood Lignin
HL	Herbaceous Lignin
PLA	Polylactic acid
PP	Polypropylene

^{o}F	Degree Fahrenheit
^{o}C	Degree Celsius
mg	Milligram
mL	Milliliter
min	Minute
h	Hour
wt%	Weight percentage

ACKNOWLEDGMENTS

First, I would like to express my highest gratitude to my advisor Dr. Xianglan Bai for offering me the opportunity to pursue a Master of Science degree in Iowa State University. I also appreciate her valuable guidance and suggestions in the past two years. I would like to thank Dr. Xinwei Wang and Dr. Eric Cochran for serving as my committee members to give me valued comments.

To Wangda Qu and Yuan Xue, I would like to say thank you both so much for offering me experiences in research design and test. I would also like to thank Yiyao Zhang, Junkai Wang and Chaoyue Huang for assisting me throughout the research work as research assistants. All your unselfish assistance made my research work more efficient. In addition, I would like to express my gratitude to all friends and academic staffs in BEI (Bioeconomy Institute), who provided me equipment access and technical support during my master study.

Finally, I would like to offer my gratitude to my family, who encouraged me all the time.

ABSTRACT

In natural world, lignin is unique and the most abundant renewable carbon source after cellulose, therefore, more applications of adding commercial value of lignin are needed. Polylactic acid (PLA), which has the second highest consumption of bioplastic in the world, is a biodegradable composite with widely application in industry. A filler adding into PLA can decrease the cost of the composite, and change the mechanical and thermal properties compared with original pure PLA. In this thesis report, the objective is to analysis how a lignin-based filler could influence the mechanical and thermal properties of PLA composite. In Chapter 2, hydrochloric acid wash was applied to reduce the ash content of Lignin from 7% to 4% and 2%. TGA, FTIR, ICP, MPT and elemental analysis tests were applied to analysis the basic properties of lignin and pure PLA. Then, lignin with 2%, 4% and 7% ash content were applied as fillers in PLA composite with 5%, 10% and 15% weight percentage, respectively. The extruded mixed composite was produced into films to test thermal and mechanical properties by TGA, FTIR and MPT tests, including decomposition temperature, tensile strength, modulus, and strain of lignin-PLA composite. Same tests were also applied in Chapter 3. In Chapter 3, lignin with 4% ash content was acetylated to remove hydroxyl group before it was added into PLA as filler to produce films. The results were compared with the ones in Chapter 2. Also, films made by pure PLA, 4% ash content and 5wt% lignin filler, and 4% ash content and 10wt% acetylated lignin filler were heated at 40^{o}C for 48 and 72 hours.

Results showed that compared to pure PLA, adding lignin-based filler would decrease tensile strength and strain, whereas increase tensile modulus and thermal stability. There is an optimum ash content in lignin as filler, high ash content in lignin could reduce both mechanical properties and thermal stability. There is probably a combined effect of lignin and inorganic ash. Samples with acetylated lignin with 4% ash content and 10% weight percentage as filler showed the highest tensile strength, which is very similar to that of pure PLA, and a more stable strain under heat treatment after 48 and 72 hours. After comparison, acetylated lignin can certain increase modulus without reducing tensile strength (up to 10wt%). Meanwhile, lignin-based fillers are able to increase hydrophobicity of the composites.

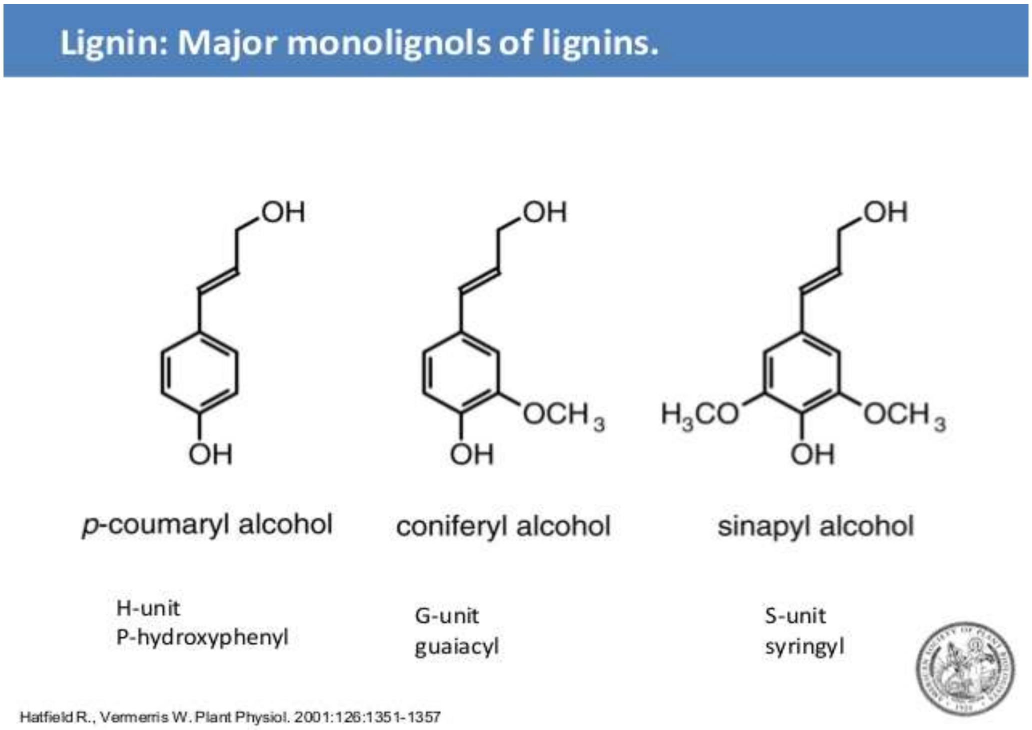
CHAPTER 1. INTRODUCTION

1.1 Lignin

A. P. de Candolle, a Swiss botanist, first described lignin as “a fibrous, tasteless material” and named this material “lignine” in 1813. [1] This was the first time that lignin was known and studied by scientists. The name “lignine” is derived from a Latin word “lignum” which means wood. Lignin is the most abundant phenolic polymer in nature, and the second most abundant renewable carbon source after cellulose. The approximate chemical formula of lignin is $(C_{31}H_{34}O_{11})_n$, and the elemental composition is 63.9% carbon, 30.2% oxygen and 5.9% hydrogen. Although the mineral content of lignin may vary depending on the biomass species, there is usually 0.7 wt% mineral components in lignin.

Lignin is a propane-phenyl-based 3-D bio-polymer consisting of three major monolignols: paracoumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which are known as H-unit, G-unit and S-unit respectively. Through bio-synthesis process, lignin were built up by the three units joined together with ether and C-C linkages. Different from the regular structure of cellulose, the physiochemical structure of lignin is much more complex, which make it impossible to identify lignin with accurate chemical formula.

The lignin content in biomass can vary in the range from 10 to 40 wt%, depending on the biomass species. Generally, the lignin content in woody biomass is higher than that in herbaceous biomass. Based on the composition of building units, lignin can be classified as hardwood, softwood and herbaceous lignins. Hardwood lignin is mainly made up of S-unit and G-unit. Softwood lignin is mostly composed of G-unit. Herbaceous lignin consists of all three monolignols and is slightly rich in H-unit, which makes its chemical properties quite different from the other two types of lignins. The chemical formula shows that lignin has a higher carbon content than cellulose does, and the energy contained in lignin can account for 1/3 energy of the whole biomass.



Hatfield R., Vermerris W. Plant Physiol. 2001:126:1351-1357

Figure 1. *Major monolignols of lignin [4]*

In pulping industry, the Kraft pulping method is the most used for the delignification of wood fibers to produce pulp and paper, at the same time generating large quantities of lignin as the by-product annually. [2] Every year, around 40 and 50 million tons of lignin is produced from the pulping industry all over the world. Moreover, the production of lignin is expected to increase considering the growth of cellulosic ethanol production. However, only 2% of lignin from industry was efficiently utilized. Due to the lack of efficient conversion technology, lignin has been viewed as a waste material and low-grade combustion fuel.

Among the three major components of biomass (cellulose, hemicellulose and lignin), lignin is the most recalcitrant part for both thermochemical and biological conversion pathways because of the condensed and irregular chemical structure. There is a saying describing the utilization of lignin that “You can make everything out of lignin, except money”.

In general, low cost fuel is one of the most widely used application of lignin. Currently, the largest amount of lignin is burned directly for energy needs. As mentioned before, lignin is the only bio-polymer containing aromatic structure, making it a potential precursor to produce chemicals, fuels and materials. Many conversion pathways have been proposed and studied for efficient utilization of lignin. For example, lignin can be predominantly converted into phenolic monomers and aromatic hydrocarbons through thermochemical pathways. The high carbon content of lignin makes it possible to use lignin as a precursor for carbon nanoparticle synthesis. Recently, there is growing interest for converting lignin into carbon fiber which is a high-value added material that can be widely used in automobile and aerospace industries. Many focuses have also been placed in the fabrication of lignin into electro-spun carbon nanofibers and other carbon based particulate nanostructures for various technological applications. [3] Another application of lignin, which has raised much interest from the public, is making lignin-based polymer composite. Most composites used nowadays are from petroleum industries. Since green-house gas emission has now become one of the most serious environmental problems, the production of composites from biorenewable resources draws attention from many researches. Considering its massive production and low cost, lignin has been viewed as one of the most potential bio-renewable resources for bio-composite production. However, there is still a long way to go to obtain lignin-derived biocomposites comparable to that from petroleum industry.

Besides, to ensure good photochemical and electrical performances of lignin derived carbon materials, most conversion processes require low level of impurities, which are mainly ash consisting of silica and metal oxides.

Figure 2. *BioChoiceTM Lignin sample*

1.2 Polylactic Acid (PLA)

Polylactic acid (PLA) was firstly synthesized by Carothers in 1932. The initial PLA had a low molecular weight and poor mechanical properties. Further improvement done by DuPont resulted in a higher-molecular-weight product that was patented in 1954. [5] In the following 40 years, the high cost of producing PLA polymers made it difficult to put PLA into practical application. Later, Cargill Dow LLC, a newly established company, facilitated the collaboration of two large companies together to focus on reducing the cost of producing PLA to gain its industrial and commercial value and made a significant success. Later they commercialized the PLA polymers under trade name NatureWorks^{TM}. In January 2002, Cargill Dow LLC built the world's only commercial production facility for PLA in Nebraska, which could produce 140,000 metric tons of PLA per year. [6]

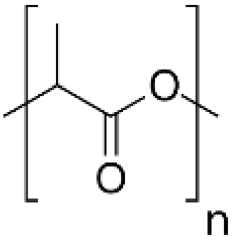


Figure 3. *General formula of PLA*

The main constitutional unit of PLA is lactic acid (LA), which has two optical configurations: L and D. In a lactic acid molecule, there are four unique groups attached to the center carbon atom, which makes the structure of the molecule chiral. L in L-lactic acid equals to left handed, and D in D-lactic acid means right handed. In L-lactic acid, hydroxy group is on the left side of the molecular formula; while in D-lactic acid, hydroxy group is on the right side. The name of PLA is based on its molecular composition. It means that PLA can be named as poly(XY-lactic acid), where X and/or Y are the amount of L- and D-lactic acid, respectively. For instance, a PLA sample with a label------poly(80% L-lactic acid) consists of 80% L-lactic acid and 20% D-lactic acid. Compared to D-lactic polymers, which is more amorphous, polymers with high level of L-lactic acid has a much better crystallinity. [6] Therefore, PLA with high L-lactic acid content is much more widely used for both researches and applications.

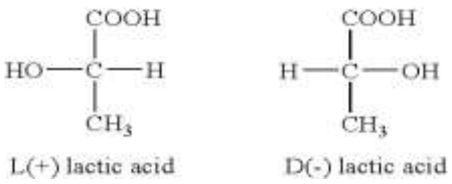


Figure 4. *Formula of L-lactic acid and D-lactic acid*

Properties of PLA varies because of the change of L/D-lactic acid content. According to the result reports from Dr. Henton and Dr. Rogers, the basic properties of PLA is shown below in *Table 1*. [7][8]

Table 1. *Basic Properties of PLA*

Technical Name	Polylactic Acid (PLA)
Chemical Formula	(C3H4O2)n
Melt Temperature	157 - 170 °C (315 - 338 °F)
Typical Injection Molding Temperature	178 - 240 °C (353 - 464 °F)
Glass Transition Temperature	44 – 63 °C (111 – 145 °F)
Heat Deflection Temperature (HDT)	49 - 52 °C (121 - 126 °F) at 0.46 MPa (66 PSI)
Tensile Strength	51 - 66 MPa (8840 - 9500 PSI)
Flexural Strength	48 - 110 MPa (6,950 - 16,000 PSI)
Specific Gravity	1.24
Shrink Rate	0.37 - 0.41% (0.0037 - 0.0041 in/in)

PLA is so popular in current market because it represents a cost-effective and non-petroleum plastic production. PLA is famous for its biodegradable property with no toxic, which can be used in food handling and medical implants. PLA can naturally degrade when exposed to the environment, for instance, a PLA bottle left in the ocean would typically degrade in 6 to 24 months. Therefore, the low cost of waste treatment attracts increasing interest in developing applications of PLA. Injection or blow molding, extrusion, fiber spinning, and thermoforming are the most popular processing possibilities of PLA as typical commercial biodegradable polymers. [9] Besides, most PLA products are ivory-white, thus it is possible for dyeing to respond to market demands.

Despite such attractive advantages, the limitation of PLA application cannot be ignored, which is the low glass transition temperature. Glass transition temperature is a very important thermal property of polymers: below T_g, polymers are hard and glassy; above T_g, polymers start to perform as soft, rubbery materials. T_g of PLA is between 44 and 63°C. This makes PLA unsuitable for high temperature applications. For instance, if the dashboard of a car is made of PLA, sunshine in summer could cause the parts to soften and deform. Consequently, study of enhancing the thermal stability and maintaining mechanical properties of PLA are necessary and popular currently.

Figure 5. *Sample of PLA filament*

1.3 Lignin-Based Polymer Composites

Polymer-based materials attracts enormous amount of research efforts for application during the last decades. Human lives are significantly improved by polymer products, and modern civilization is greatly influenced in every aspect by the invention of polymers. To satisfy the demand of market and achieve a higher market value, research of polymer materials need to improve the mechanical and/or thermal properties, and reduce the cost of production. Back to 1960’s, the idea of using lignin as fillers or reinforcements in thermoplastic materials was started. However, there was not much progress in bringing the research idea into application. The interest of lignin has been renewed in recent years. [10] Lignin, the second most abundant biopolymer on earth, could possibly reduce the cost of polymer composite production and improve biodegradability when it is used as an extender. Adding lignin into PLA or Polypropylene (PP) are popular topics in the last decade, and the lignin under research is mainly Kraft lignin.

1.3.1 Lignin-Polypropylene Composites [10]

In Dr. Toriz's research, Kraft lignin produced by Westvaco Co. was added into polypropylene (PP) as a filler. The lignin was purified by removing all hemicellulosic materials, and the lignin purity reached 97% on dry basis. The temperature of melt mixing was controlled at 170 °C, in case that a higher temperature could degrade lignin. Samples were molding to specimens according to ASTM standard tests for plastics.

The weight percentage (wt%) of lignin in composites was started from 0% to 60%, increasing by 10% in each test. Correspondingly, the tensile strength decreased with the addition of lignin, which was from 35.92 MPa to 14.36 MPa. It is reasonable considering a poor adhesion between the two components, which could lead to an increasing chance of mechanical failure. On the other hand, Young's modulus of the composites was increasing as soon as the weight percentage of lignin reached 10 wt% and stopped increasing at 30 wt%; from 40 wt% Young's modulus started to decline again. There seems a limit of weight percentage of lignin added in PP, where the increasing interaction between lignin and composites stopped.

The research also showed that if mineral fillers were added into PP with lignin, the properties improved compared to lignin-only filler, which might be due to a better interaction between lignin and PP and/or a better lignin particle distribution. Further study about the ratio of mineral filler which could optimize the properties is still needed.

1.3.2 Thermal, Dynamic Mechanical Properties of PLA-lignin [11]

In Dr. Muhammad's research, Kraft lignin from Innventia and tannin from Silva Chimica were used as fillers in PLA made by NatureWorks LLC. In this thesis report, only lignin-filler groups will be discussed.

Including pure PLA (lignin wt%=0), there were four groups with weight percentage of lignin of 0wt%, 5wt%, 10wt%, and 15wt% in the composites, respectively. Before melting mixed with PLA, lignin was vacuum dried at 40^{o}C for more than 48 hours. Melting mix was conducted at 185 °C for 5 minutes. A mini injection molding equipment was used to make standard dog-bone-shape samples.

Scanning electron microscopy (SEM) results showed that along with the increase of lignin weight percentage, clearer matrix-filler interfaces was manifested. The phenomenon showed in SEM results was corresponding to the results got from mechanical property tests: additional lignin filler would decrease the tensile strength compared to pure lignin. From the Differential scanning calorimetry (DSC) results, it was shown lignin played a role of inhibition on the crystallization of PLA-Lignin composites. Also, degradation of PLA-Lignin occurred at a slightly lower temperature than pure PLA. As a conclusion, lignin-based filler can influence both thermal and mechanical properties of PLA. Further research about how to improve the properties are needed.

1.3.3 Properties of Composites with Acetylated Lignin-filler [12]

Dr. Gordobil used commercial alkali lignin (CL) as the filler to determine PLA-Lignin composites' degradation and stability. Different from Dr. Mohammad's research, half of lignin was added as filler directly, and another half in this project was acetylated as pre-treatment. For the procedure of acetylation, lignin was dispersed in form amide with a concentration of 1g/25mL for 3 hours. After a complete solubilization, 40mL pyridine and 6.6mL acetic acid anhydride were added. Before another 6.6mL acetic anhydride was added, solution was stirred at room temperature for 3 hours, followed by same amount of acetic anhydride after another 3 hours. Acetylated lignin was washed by deionized water and diethyl-ether, and then dried at 50^{o}C for 24 hours in an oven.

Acetylated lignin and PLA were mixed at 200^{o}C for 10 minutes in an extruder. The concentrations of both Kraft lignin and acetylated Kraft lignin were 0.5wt%, 1wt%, 5wt%, 10wt%, and 20wt%. Samples for mechanical testing were 6 cm long with a thickness between 0.15 and 0.25 mm, and a width between 2.5 and 5 mm. Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), Thermogravimetric Analysis (TGA), and mechanical properties test were applied.

By comparing the FTIR results of both Kraft lignin and acetylated Kraft lignin, there were two clear change: the curve turned flat at 3300cm^{-1} and new peak occurred at 1750cm^{-1}.

The signal at 3300cm^{-1} indicates aromatic and aliphatic O-H group, and the signal at 1750cm^{-1} indicates ester bond. In acetylate Kraft lignin's chart, it showed that the signal at 3300cm^{-1} was reduced almost completely, which means the acetylation was successful.

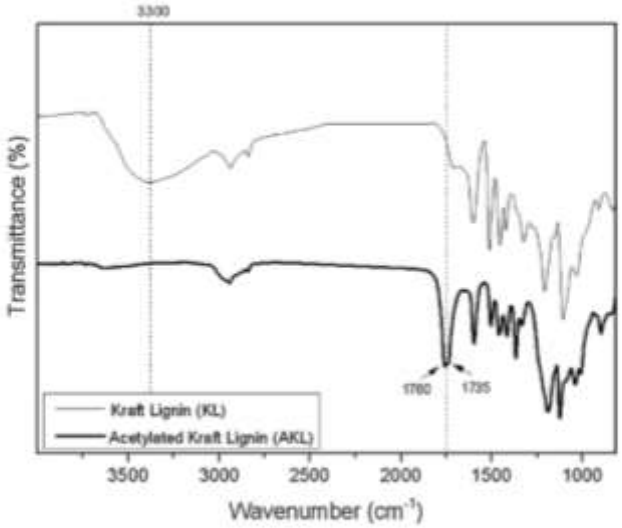


Figure 6. *FTIR of Kraft Lignin and Acetylated Kraft Lignin*

In DSC result, it was obvious that acetylated Kraft lignin has a lower T_g than Kraft lignin without acetylation. The reason could be that hydroxyl groups were replaced by ester substituent during acetylation, thus, increased free volume on the molecule would occur because of the reduction of hydrogen bonding. Through Thermogravimetric Analysis (TGA) test, the maximum weight loss temperatures (T_{max}) of the samples with filler were all increased by comparing to pure PLA, which is a proof of that the addition of different lignin could increase thermal stability.

In the result of mechanical properties, tensile strength of Lignin/PLA without acetylation samples was decreasing rapidly with increasing lignin content when the concentration was higher than 5wt%. For Lignin/PLA with acetylation samples, tensile strength decreased slower than before. Moreover, the deformation at break point (%)

decreased as the untreated lignin weight percentage increased from 1wt%. While, there can be seen an increase in deformation of all samples with acetylated lignin.

As a conclusion, lignin-based filler was successful in increasing $T_{max,}$ which indicates a more stable thermal property; acetylated-lignin filler performed better than original-lignin filler in keep tensile strength from decreasing, especially when the concentration was high. In all cases, the deformation at break was increased.

1.4 Acetylation

Acetylation is one of the most widely used chemical pre-treatments in producing lignin-based filler for polymers. Since lignin molecule contains hydroxy groups, while PLA is aliphatic polyester, which makes it hard to achieve a uniform distribution for a Lignin/PLA mixture, thus, influences the mechanical property. During acetylation process, hydroxy groups would be replaced by acetoxy groups by introducing acetyl groups. Lignin is acetylated to increase the affinity with biopolymers, such as PLA, and to prevent a deterioration of the mechanical properties.

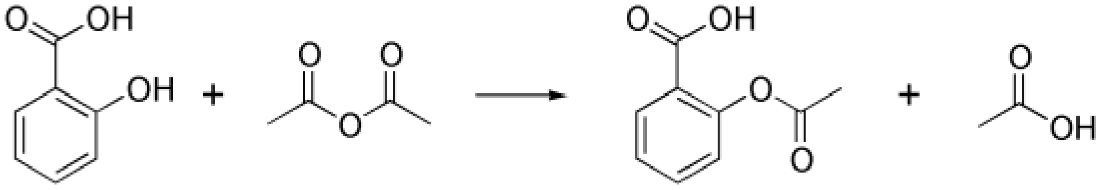


Figure 7. *An example of acetylation reaction (not lignin)*

Acetylation result can be showed on FTIR graph. In *Figure 6 FTIR of Kraft Lignin and Acetylated Kraft Lignin*, the slope of the curve at 3300 became gentle after acetylation, which means hydroxy groups were replaced; while a new peak occurred at around 1750, which indicates the introduction of acetyl groups. Figure 7 is a standard example of lignin acetylation.

1.5 Objectives of the Project

Lignin is always used as a low-cost energy resource. Since both lignin and PLA are biodegradable, it is exercisable to produce Lignin/PLA composite to decline the cost of PLA products.

The objectives of the project are:

(1) Investigate potential of using corn stover lignin as a filler in PLA composite;

(2) Explore how inorganic ash in lignin influences the thermal and/or mechanical properties of PLA composites;

(3) Investigate how acetylated corn stover lignin filler influences the thermal and/or mechanical properties of PLA composites.

CHAPTER 2. LIGNIN FILLERS IN PLA: The EFFECTS OF IMPURITIES IN LIGNIN

2.1 Overview

It is saying that: you can use lignin to make everything but money. Lignin is biodegradable and always available as byproduct from pulp and paper industry and emerging cellulosic biorefineries. [13] Usually, lignin, which has been used in other researches, is hardwood or softwood lignin with a high purity. Since silicates are not soluble and calcium salts have a lower solubility in acidic solution [14], which rises the cost to wash lignin to achieve a low ash content. The lignin used in this project is corn stover organosolv lignin made by Archer Daniel Midland Company (ADM). Different from other researches, which used hardwood lignin or softwood lignin, ADM lignin used in this project is herbaceous lignin from biorefinery, which is always used as a low-cost fuel. Compared to hardwood lignin and softwood lignin, molecular structure of herbaceous lignin is unique because of paracoumaryl alcohol (H-unit). Also, inorganic ash content in corn stover lignin is relatively higher than highly purified hardwood or softwood lignin. Thus, study of using herbaceous lignin with a relatively lower purity as filler to improve thermal and/or mechanical properties of biopolymers is the specialty of this project.

PLA is a biodegradable thermoplastic with no toxic, which is always used as food handling and medical implants. Compared to PP, PLA has a higher flexural modulus and flexural strength. Maintaining the degradable characteristic of PLA is the premise of injecting filler into matrix to improve thermal and/or mechanical properties of PLA.

Furthermore, the cost of lignin can be negligible. The cost of PLA products will be definitely decreased by adding lignin. The PLA used in this project is NatureWorks Ingeo Polylactic acid 6260D.

2.2 Experiment Preparation

In Chapter 2, lignin was washed to decrease the content of impurity before producing Lignin/PLA composites. No acetylation treatment was applied in Chapter 2.

2.2.1 Lignin Preparation

The ADM lignin used in this project was isolated from corn stover by organosolv process, therefore, minerals as well as hemicelluloses are common impurities in commercial lignin. Thus, washing lignin to control ash content is necessary prior to experiments.

Approximately 30 grams of the fine brown lignin powder were ball milled at 400 rpm for 30 minutes, where it changed direction of spinning every 5 minutes interval. The milled lignin was washed with 300mL of 0.1N hydrochloric acid by stirring at 600 rpm for 30 minutes. The stirring process was operated in a beaker using a magnetic stirrer. The acid solution and lignin mixture were filtered through a 70mm Whatman GF/F glass microfiber filter under vacuum. Three times of water wash by deionized water were repeated after the almost dry lignin was collected. The lignin was dried in an oven at 40^{o}C overnight. In order to maximize the surface area, lignin was spread out on a watch glass. Before use, lignin was ball milled at 400 rpm for another 30 minutes.

Ash content of raw ADM lignin before wash is 7%. Controlling reaction atmosphere of lignin wash can achieve different ash content level. Lignin wash was operated by Junkai Wang and Yuan Xue, and ash contents of washed lignin were controlled at 4% and 2%, respectively. Therefore, there are totally three lignin samples with different ash content (2%, 4% and 7%) using in this project, and for convenience, they are named L(2% ash content, Low ash content), M(4% ash content, Medium ash content), and H(7% ash content, High ash content). Since there is not a sharp chemical reaction during washing process, no obvious difference on appearance between each lignin with different ash content.

Figure 8. *Left: L lignin; Right: H lignin (raw ADM lignin)*

2.2.2 Lignin/PLA composite preparation

Lignin/PLA blends were prepared by melting extruding with a twin-screw microcompounder (DACA Instruments, Santa Barbara, CA). Precursors were fed into the microcompounder through A. There are two heaters inside part B and C, the temperatures of which can be controlled by two separated heater controllers, therefore, temperatures on both sides can be set differently. In this project, temperatures of B and C are set equally. Upper temperature shown on the screen of controller is the actual temperature, and the one shown below it is the set temperature. Mixture exits the microcompounder through D. Speed of drills are set at the right bottom corner.

Figure 9. *Picture of microcompounder*

The microcompounder was preheated to 200^{o}C before mixing precursors. The melting temperature of PLA is 157-170^{o}C, therefore, in the first attempt, temperature of microcompounder was set to 170^{o}C and mixed for 10 minutes. While, the film made by that mixture showed a uniformity of lignin distribution. Stripes could be seen clearly on the film. Therefore, the temperature was increased to 200^{o}C and mixing time was increased to 20 minutes. By adding mixing temperature and time, an enhanced fluidity of PLA could lead to a more uniform distribution of lignin filler. Speed of the drills is 200RPM.

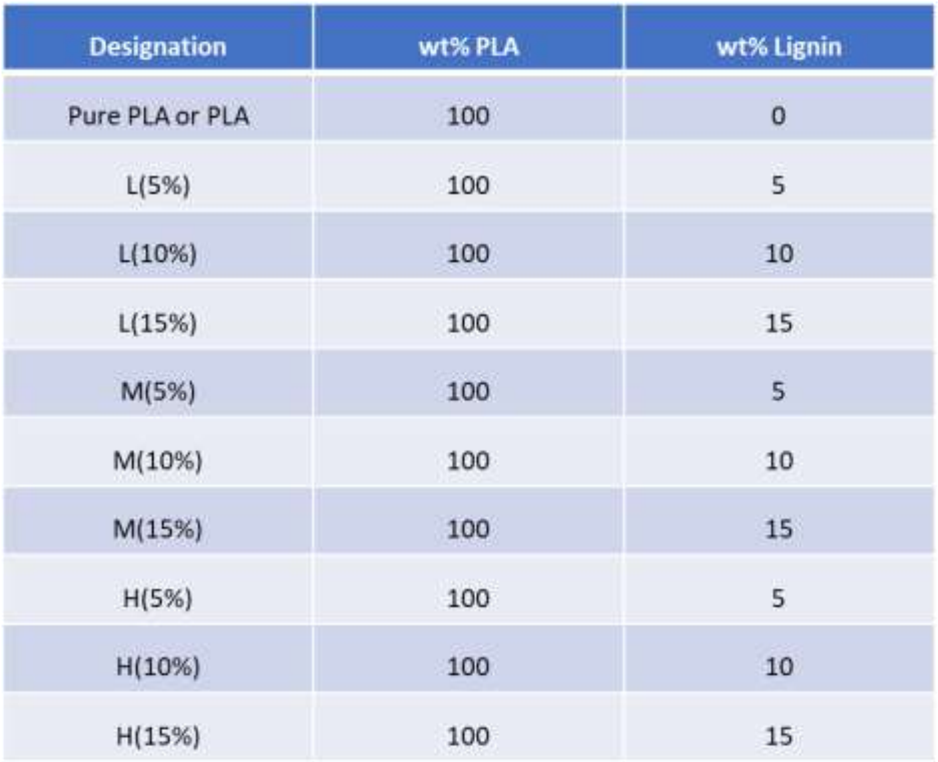
About 4 grams of PLA was fed into the microcompounder in each experiment as matrix. Fillers of different weight percentages of lignin with different ash content were added into the microcompounder during mixing. Unlike other reported researches, weight percentage of lignin in this project is not based on the final composites, it is based on PLA weight instead. Therefore, weights of PLA in each experiment are same, weight of lignin and lignin type are variables.

Figure 10. *NatureWorks Ingeo Polylactic acid 6260D*

After blending, Lignin/PLA composite is collected and prepared for producing composite film for testing. The micocompounder is cleaned as soon as the experiment finishes, in case that the composite stuck on the inner surface of the microcompounder and pollute experiments with other materials.

For instance, L(5%) is made by 4 grams of PLA, and 5%*4grams=0.2gram of 2% ash content lignin. For convenience, *Table 2* highlights the composition of the composites in each experiment.

Table 2. *Composition of Lignin/PLA composites*



Designation	wt% PLA	wt% Lignin
Pure PLA or PLA	100	0
L(5%)	100	5
L(10%)	100	10
L(15%)	100	15
M(5%)	100	5
M(10%)	100	10
M(15%)	100	15
H(5%)	100	5
H(10%)	100	10
H(15%)	100	15

2.2.3 Lignin/PLA Composite Film Preparation

Lignin/PLA composite film is made by Carver furnace with heat pressing. Prior to increasing the temperature, a flat metal sheet is placed on the lower heater of the furnace, covered by a Teflon sheet with almost the same size of the metal sheet. After composite mixture is melting, put another Teflon sheet and a flat metal sheet on the top of it, which is to make sure that: 1. the composite film can be removed without damage after heat pressing;

2.the pressure can be applied evenly on the composite mixture so that the thickness of the film is uniform.

There are two temperature controllers in the furnace, each of which can adjust the temperatures of the corresponding platen (upper is 1 and lower is 2) of the furnace. The temperatures shown on the screen of the furnace is in Fahrenheit degree, therefore, temperatures are set to 392^{o}F, which is equal to 200^{o}C, the temperature during mixing. Since the temperature increasing rate will slow down a lot when the actual temperature is close to the set temperature, therefore, in order to shorten the heating process, temperature is set to 412^{o}F first and back to 392^{o}F when actual temperature reaches approximate 390^{o}F.

Pressure is applied after the temperatures of both heaters reach 392^{o}C. Pressure is set to 1 metric tons. After 5 minutes, heaters are turned off. After the temperature decreased to 140^{o}F, which is the glass transition temperature of PLA, film can be withdrew from the furnace. The thickness is 0.15 ± 0.05 mm. The film is cut into strips with 5 ± 1mm width.

Figure 11. *Picture of Carver furnace*

Figure 12 shows an example of Lignin/PLA composite film, which was just collected from Carver furnace. Macroscopic distribution of filler in the composite is uniform.

Figure 12. *Sample of Lignin/PLA composite film (M 5%)*

2.3 Results and Discussion

Testing results of lignin precursors and Lignin/PLA composite will be discussed in this chapter. Elemental Analysis, Inductively Coupled Plasma Mass Spectrometry (ICP MS), ThermoGravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), mechanical property tests, contact angle measurement, and Morphology tests are applied.

2.3.1 Tests Results for Lignin and Discussion

Elemental Analysis

Elemental analysis was employed prior to other tests, which can help to determine the content of nitrogen, carbon, hydrogen, and sulfur. Three repeats were applied, and an average value was adopted. Results are presented in *Table 3*, which showed that ash content decreases along with carbon content increased. Therefore, it can be speculated that ash, or impurity, which has been washed is mainly inorganic. Small errors during experiments are neglectable.

Table 3. *Elemental Analysis Result (%)*

	N	C	H	S
L Lignin	1.490	59.073	4.840	0.153
M Lignin	1.433	58.057	5.084	0.153
H Lignin	1.293	54.297	4.809	0.201

ICP MS

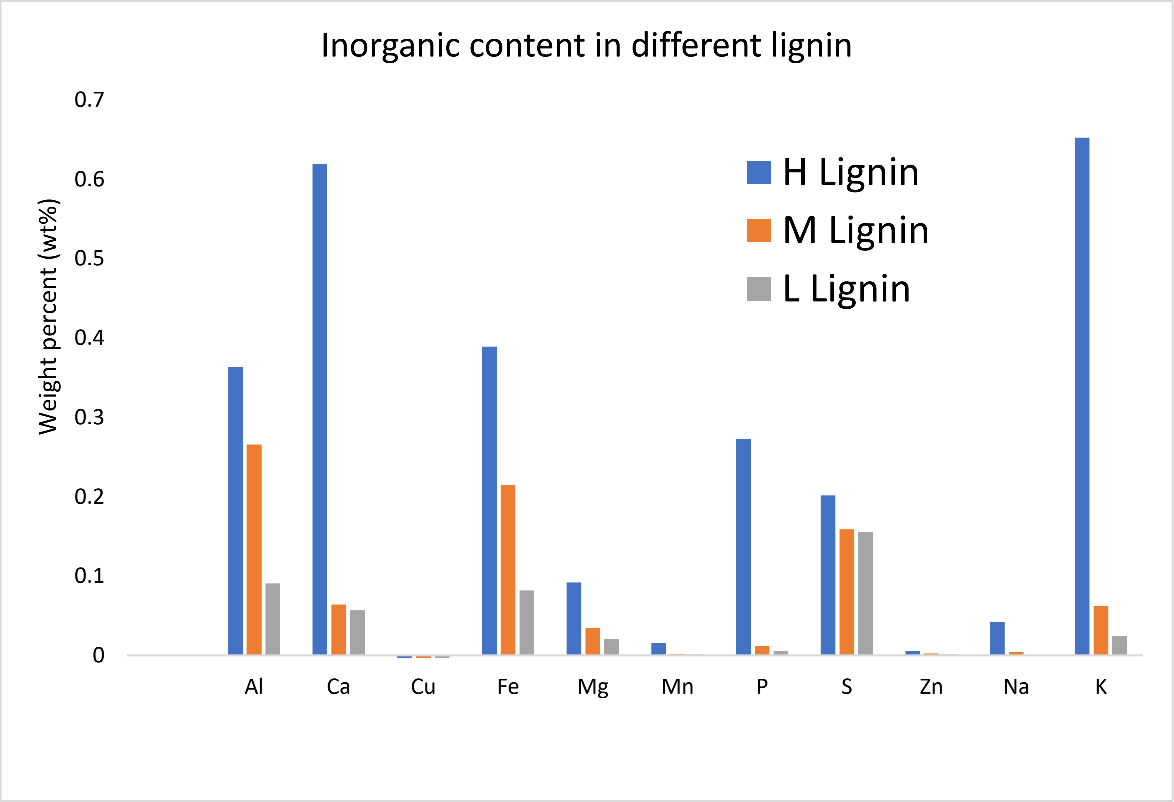


Figure 13. *Inorganic content in different lignin*

The cation quantification of lignin is determined by Inductively Coupled Plasma-Mass Spectrometer (ICP MS). Prior to quantification, lignin samples were digested following ASTM D6349 method. ICP MS results are presented in *Figure 13*. Generally, the reduction rates of all inorganic contents are proportion to ash contents of lignin. Since ADM lignin was produced with some complex impurities, some of inorganic salts are difficult to be removed perfectly. After comparison, Sulfur is the one which is relatively most difficult to be removed.

FTIR

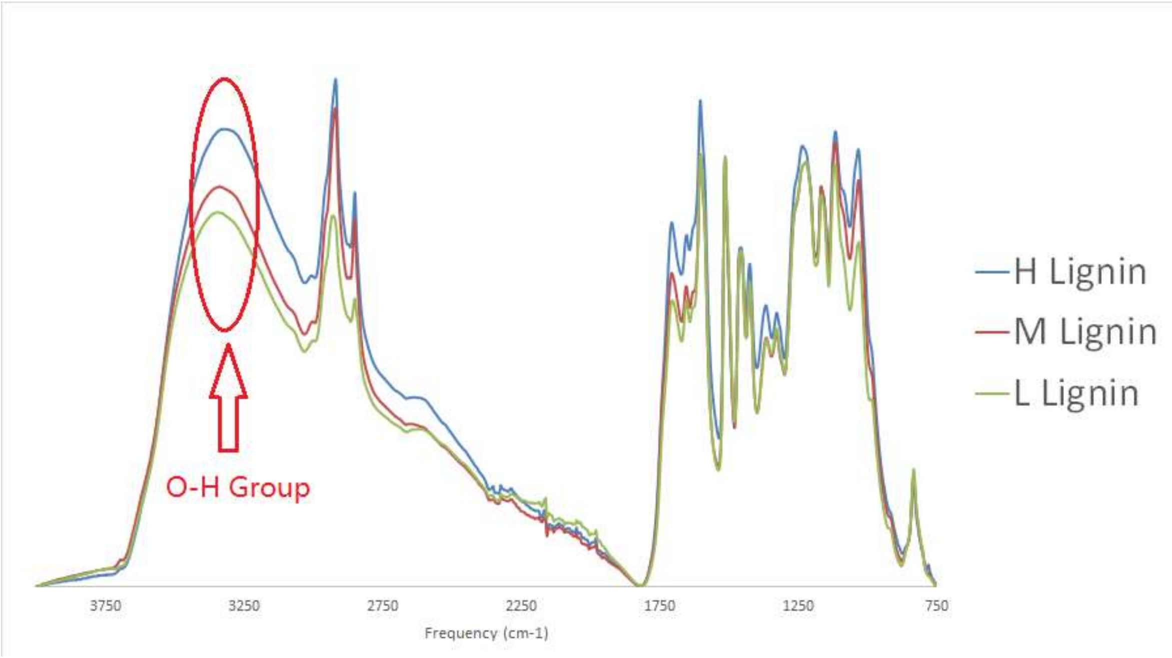
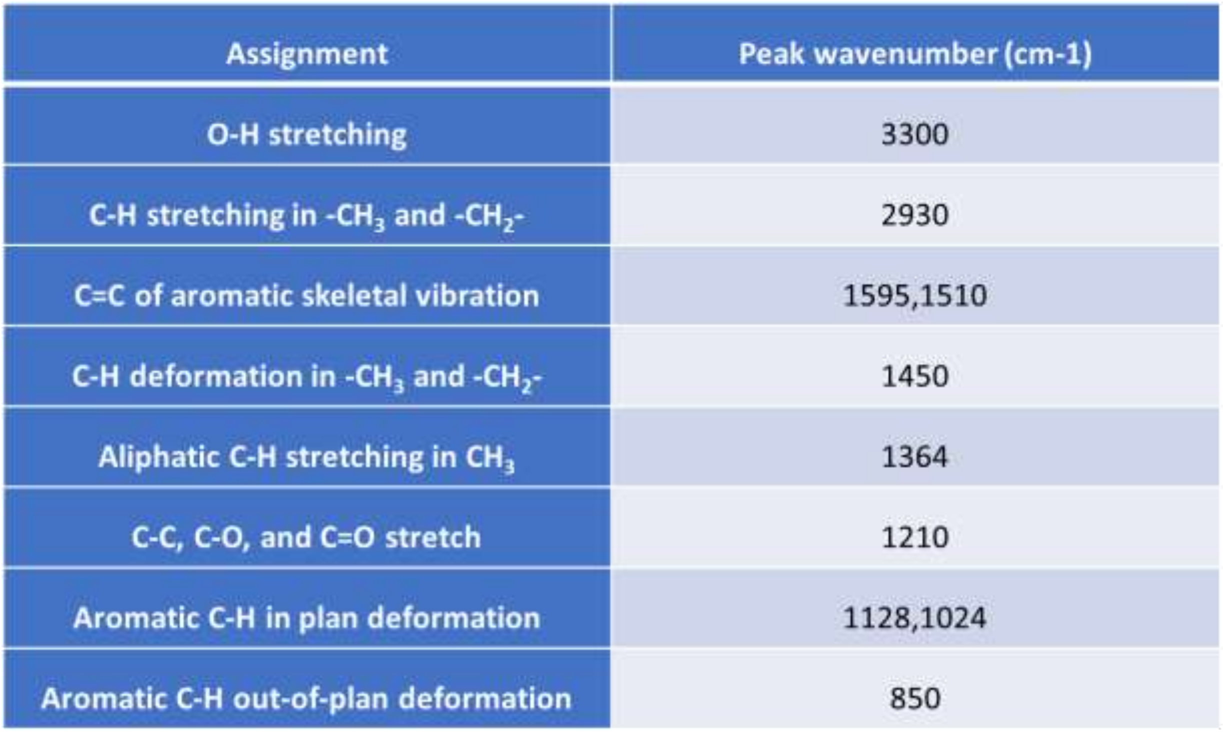


Figure 14. *FTIR results for lignin*

Results of FTIR for lignin tests are presented in *Figure 14*, Asphalt Method was employed in this project. Generally, the spectra of all three lignin are similar. The waves at 3300 showed differences, where the spectra indicate hydroxy group. Magnitude of spectra decreased with declination of ash content, which is because some hydroxy groups were washed up during lignin washing process. Even so, compared to spectra of other groups, hydroxy group expresses a very high content. Since lignin molecule contains hydroxy groups, while PLA is aliphatic polyester, which makes it hard to achieve a uniform distribution for a Lignin/PLA mixture (**1.4 Acetylation**). This chapter is focusing on how untreated lignin-based filler can influence the Lignin/PLA composite. In next chapter, acetylated lignin will be used as filler for a further study. The wavenumbers and important bands identifications of lignin are shown in *Table 4.*

Table 4. *Bands assignments of lignin FTIR result*



Assignment	Peak wavenumber (cm-1)
O-H stretching	3300
C-H stretching in -CH_3 and -CH_2-	2930
C=C of aromatic skeletal vibration	1595,1510
C-H deformation in -CH_3 and -CH_2-	1450
Aliphatic C-H stretching in CH_3	1364
C-C, C-O, and C=O stretch	1210
Aromatic C-H in plan deformation	1128,1024
Aromatic C-H out-of-plan deformation	850

TGA

TGA results were collected by TGA/DSC STAR System (Mettler Toledo) in this project. Samples were heated up from 25^{o}C to 900^{o}C by 10^{o}C/min in nitrogen atmosphere Temperature stays at 900^{o}C for 10 more minutes in nitrogen atmosphere and then atmosphere changes to air so that all organic content can be burnt in order to determine the inorganic content. Results of TGA test are presented in *Figure 15*. The inorganic ash contents of each lignin samples are obtained by burn, which are approximate 7%, 4%, and 2%, respectively. Between room temperature and 140^{o}C, three curves were almost coincidence; at 140^{o}C, a faster mass loss of lignin with 7% ash content occurred, then lignin with 4% ash content, and the last one was lignin with 2% ash content. Combined with inorganic ash contents result, it can be inferred that inorganic content can catalyze the degradation of lignin.

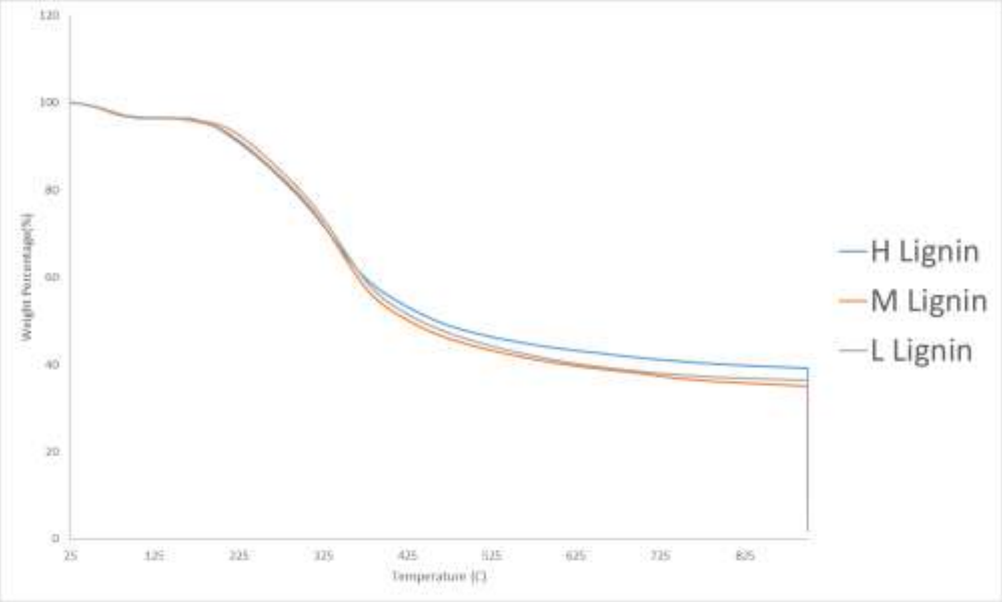


Figure 15. *TGA results for lignin*

2.3.2 Tests Results for Lignin/PLA Composite and Discussion

There are two primary variables in Lignin/PLA composite: lignin type, which is expressed by ash content, and weight percentage. In *Table* 2, shortened forms of composites are listed. The results in **Chapter 2.3.2** can be separated into two parts based on fixed variables. In part 1, composites made by same lignin, different weight percentages will be discussed; in part 2, composites made by lignin with different ash content at same weight percentage will be discussed.

Part 1 Results

FTIR

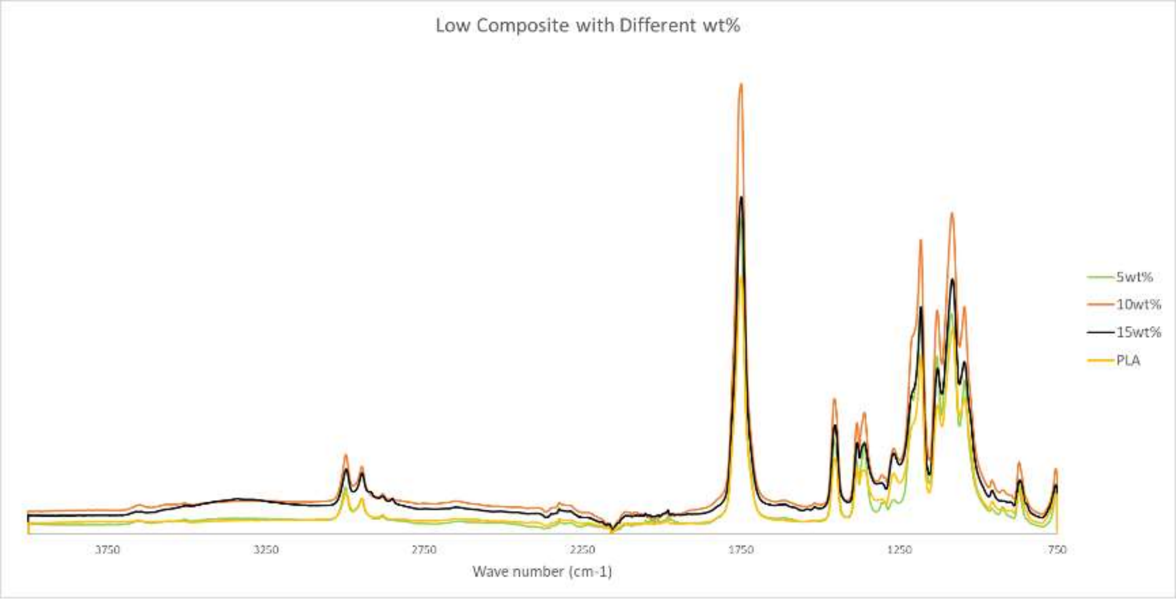


Figure 16. *FTIR results for L lignin/pla composite*

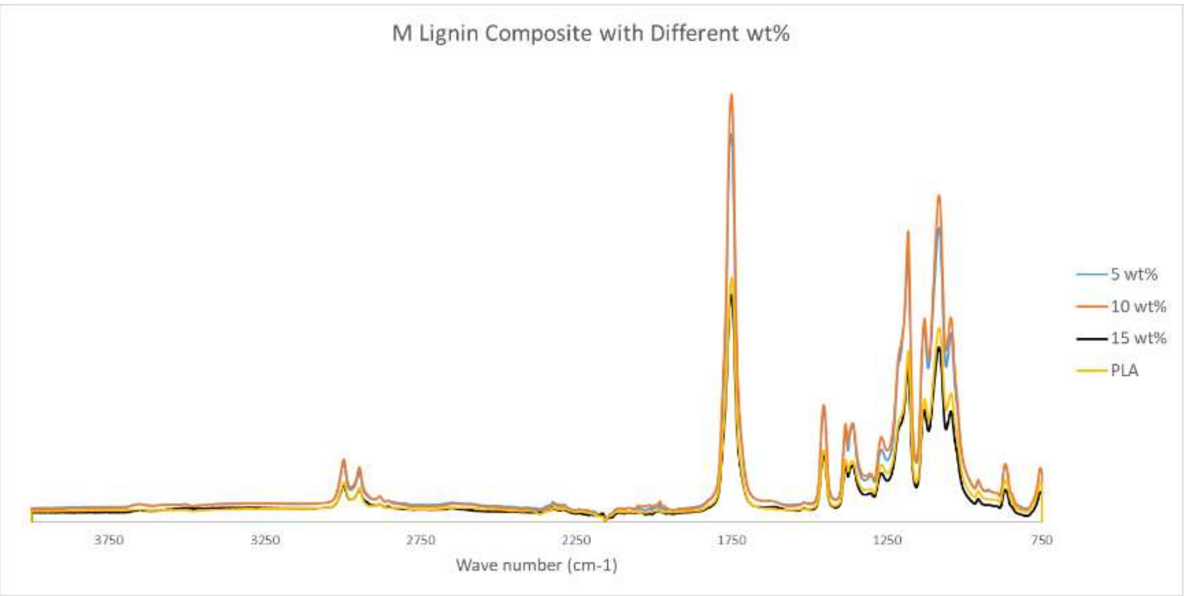


Figure 17. *FTIR results for M lignin/pla composite*

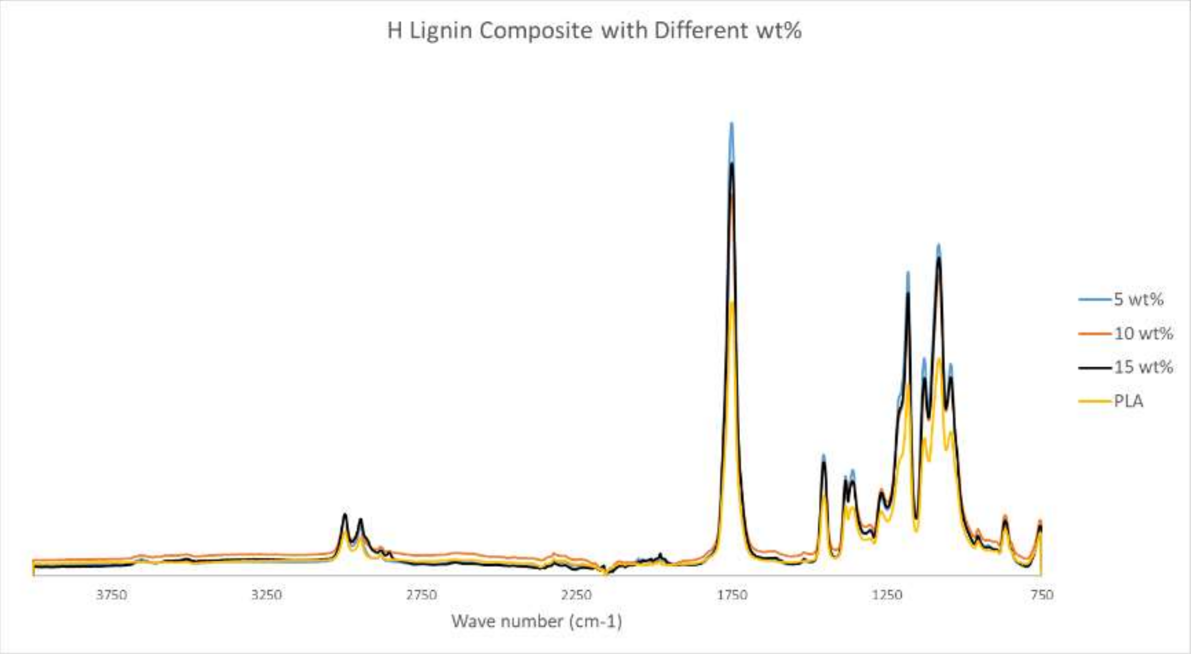


Figure 18. *FTIR results for H lignin/pla composite*

TGA/DTG

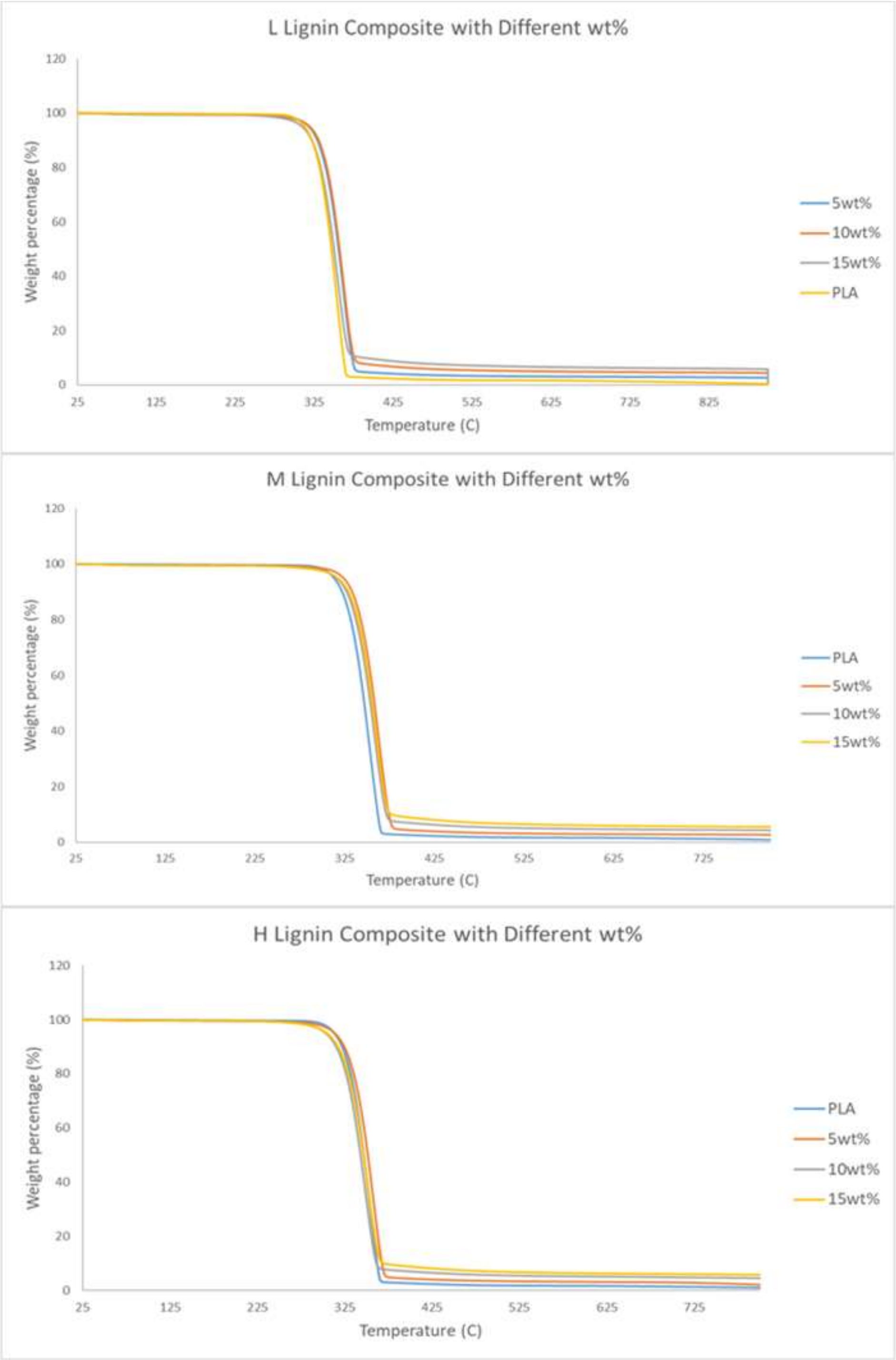


Figure 19. *TG curves for each type of lignin at different wt%*

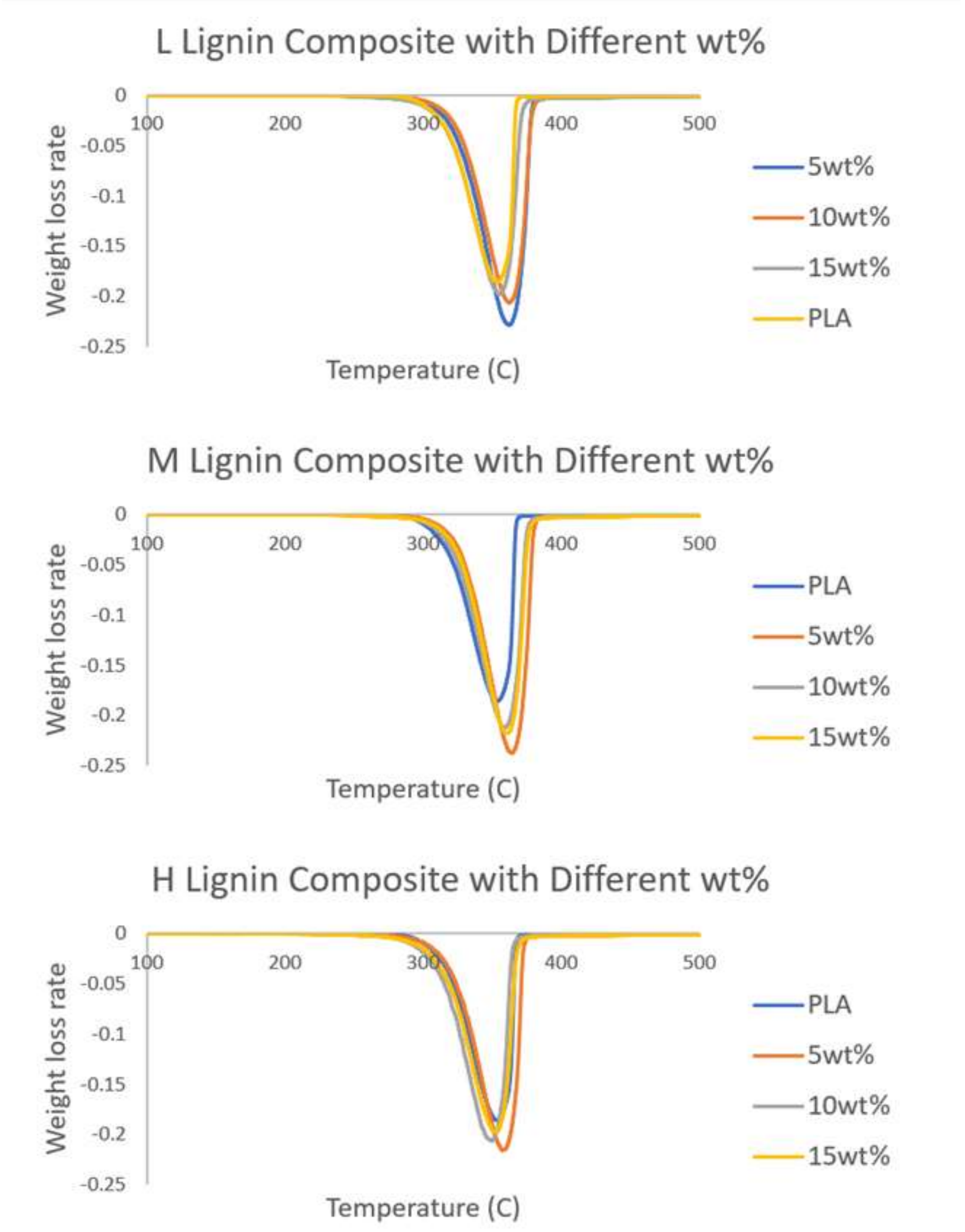


Figure 20. *DTG curves for each type of lignin at different wt%*

Mechanical Properties

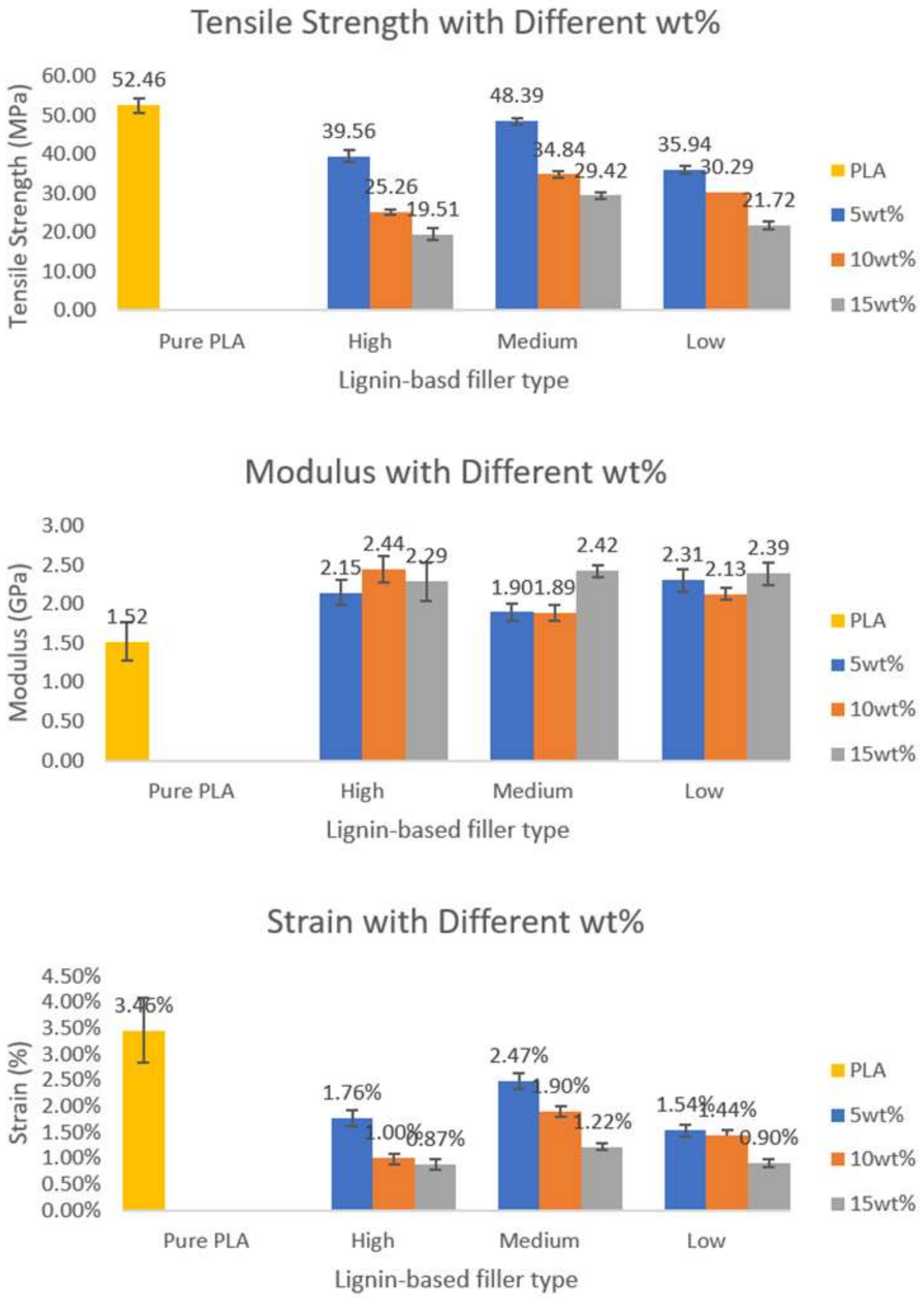


Figure 21. *Tensile strength, modulus and strain of composite based on lignin ash content change*

Part 2 Results

FTIR

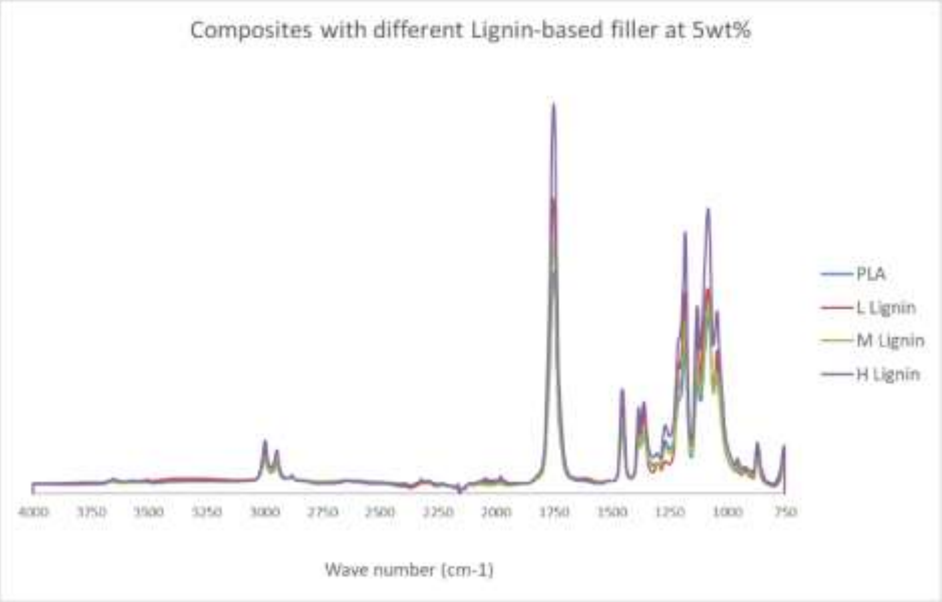


Figure 22. *FTIR results for composites with different lignin at 5wt%*

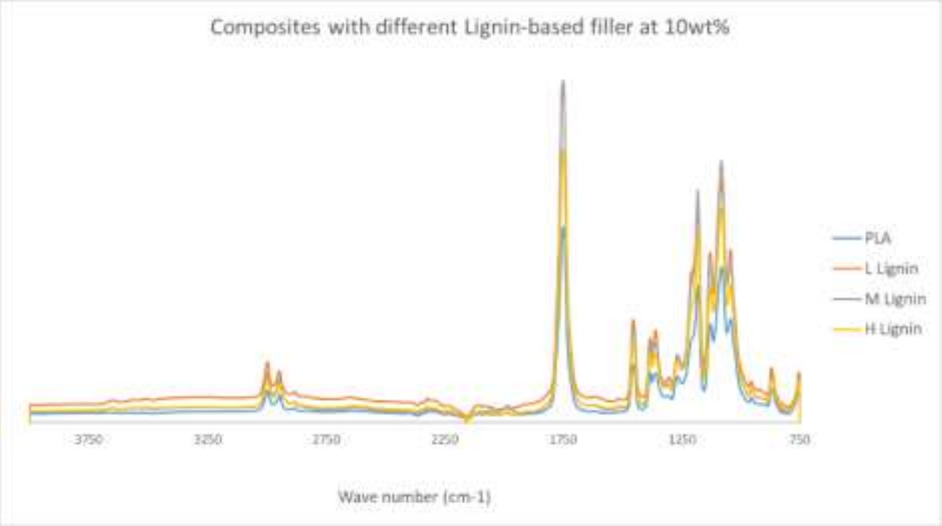


Figure 23. *FTIR results for composites with different lignin at 10wt%*

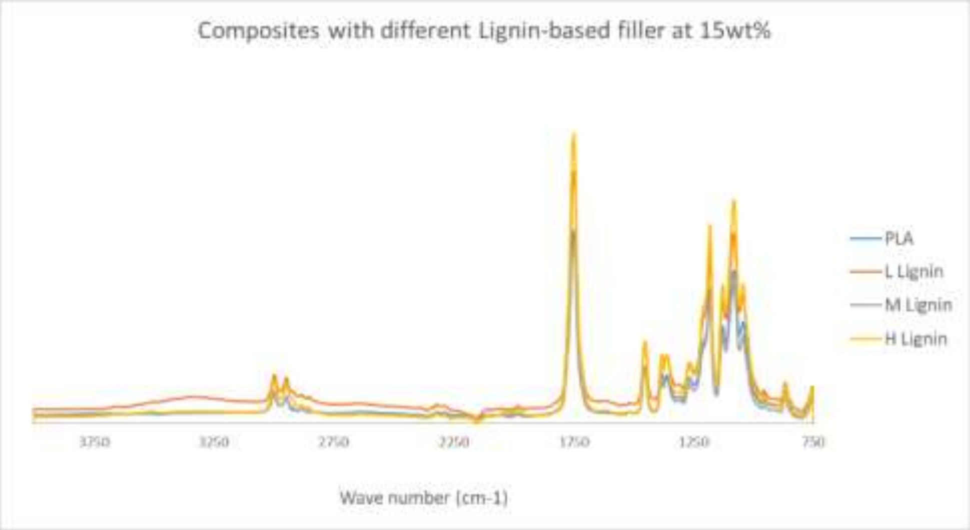


Figure 24. *FTIR results for composites with different lignin at 15wt%*

TGA/DTG

Table 5. *Td, Tmax and char residue of PLA, lignin, and composites*

		T_d (5% mass loss) (℃)	T_{max} (℃)	Char residue at 900 ℃ (%)
PLA		313.3	353.7	0.32
Lignin	(L)	200.7	350.3	36.39 (include ash)
	(M)	191.0	342	35.06
	(H)	180.0	335.5	36.75
Composite	L(5%)	318.7	362.3	2.61
	L(10%)	319.7	362.2	4.41
	L(15%)	310.2	355	5.77
	M(5%)	323.7	364.2	2.53
	M(10%)	316.5	358.8	4.00
	M(15%)	317.3	360.5	5.26
	H(5%)	313.8	357.2	1.05
	H(10%)	303.5	349.7	3.99
	H(15%)	304.7	352.5	5.34

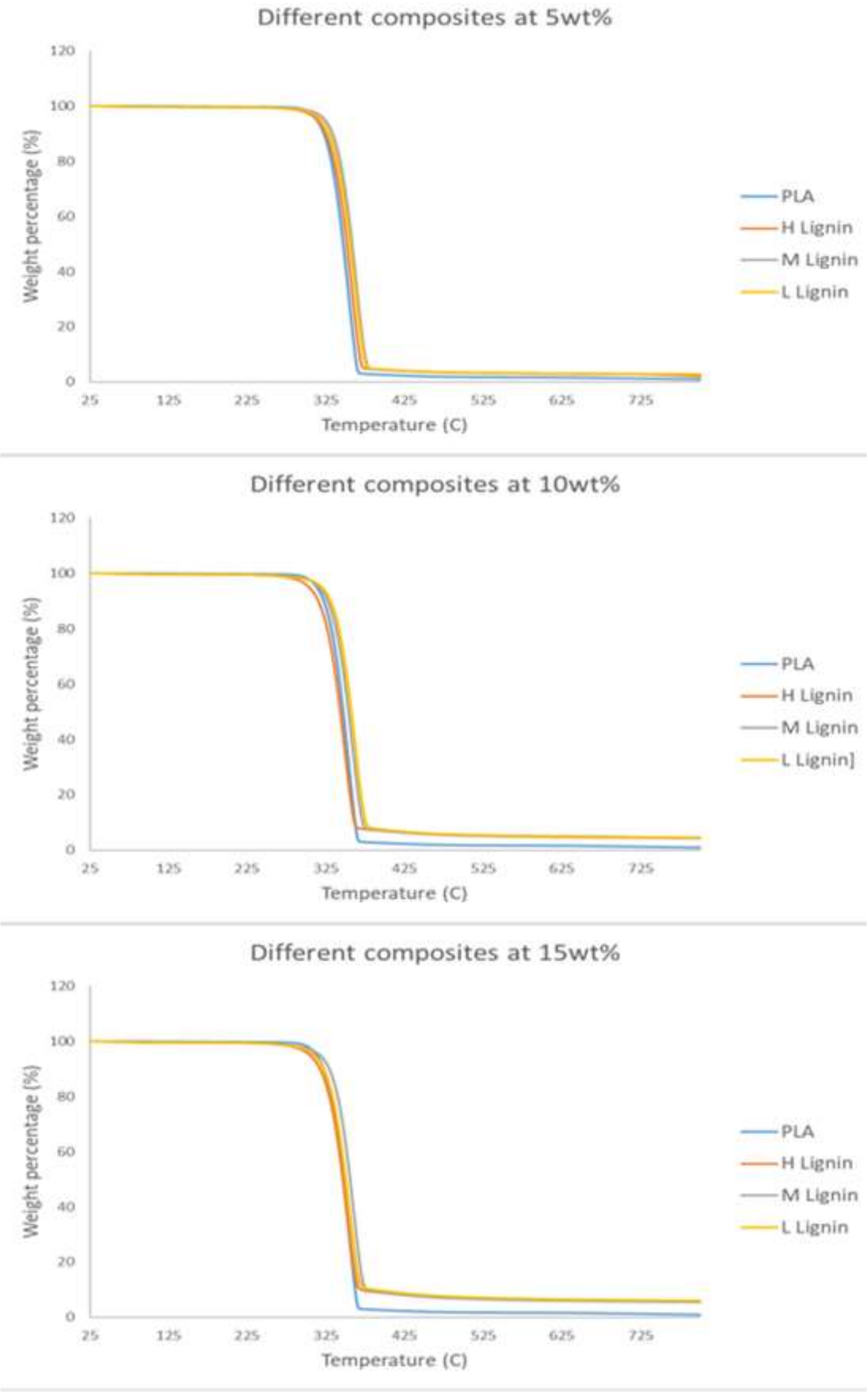


Figure 25. *TG curves for different lignin at same wt%*

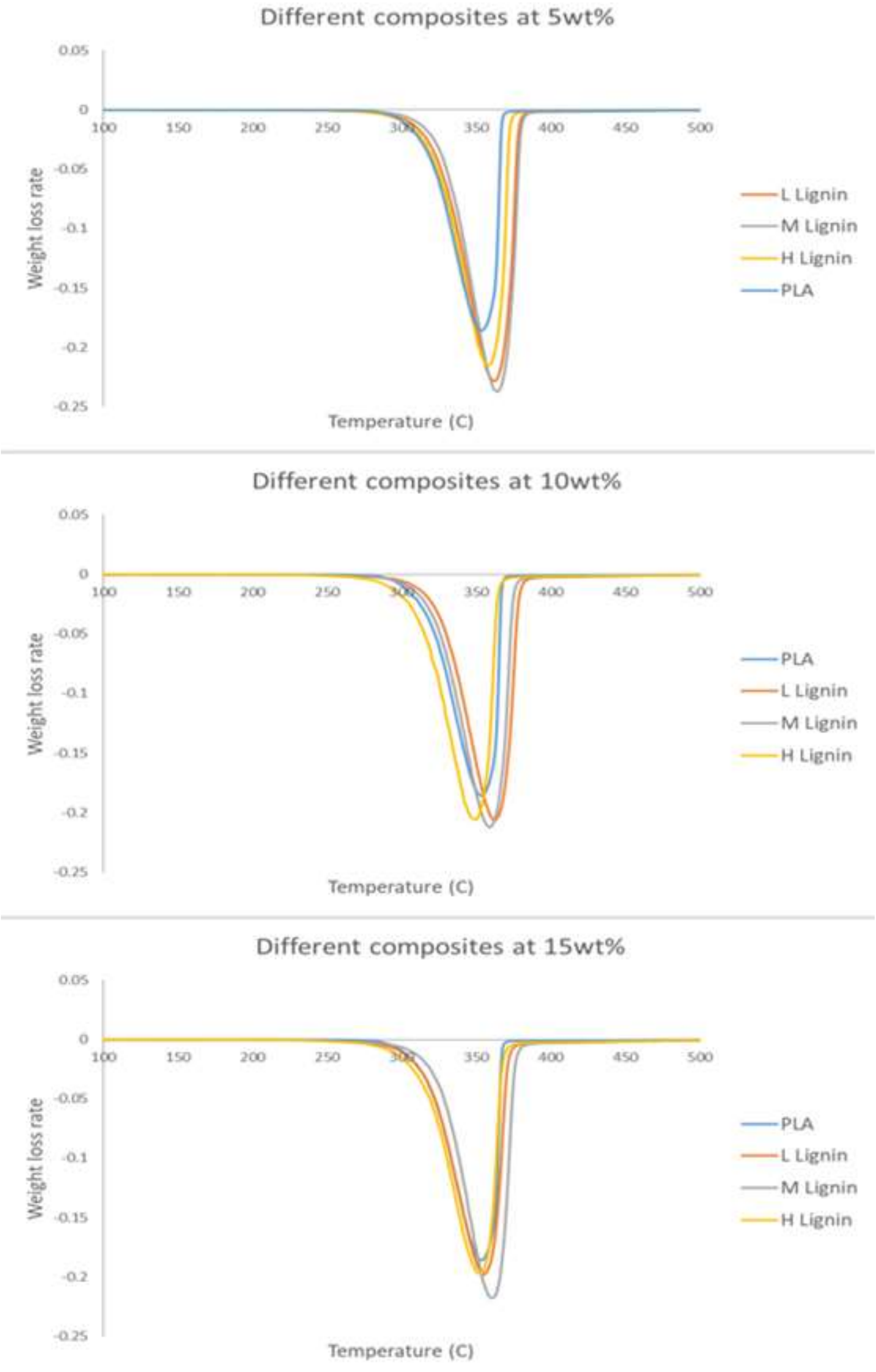


Figure 26. *DTG curves for different lignin at same wt%*

Mechanical properties

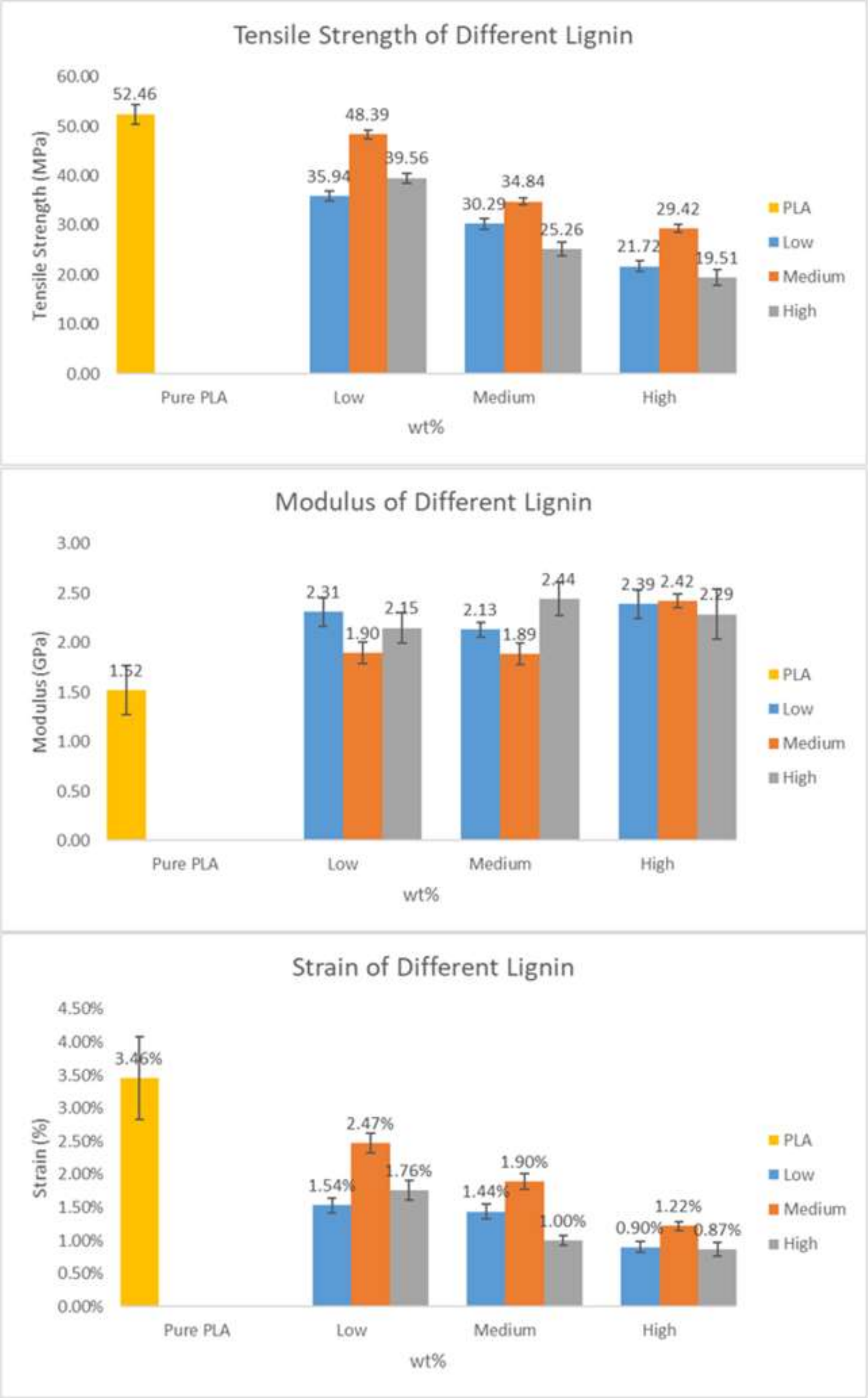


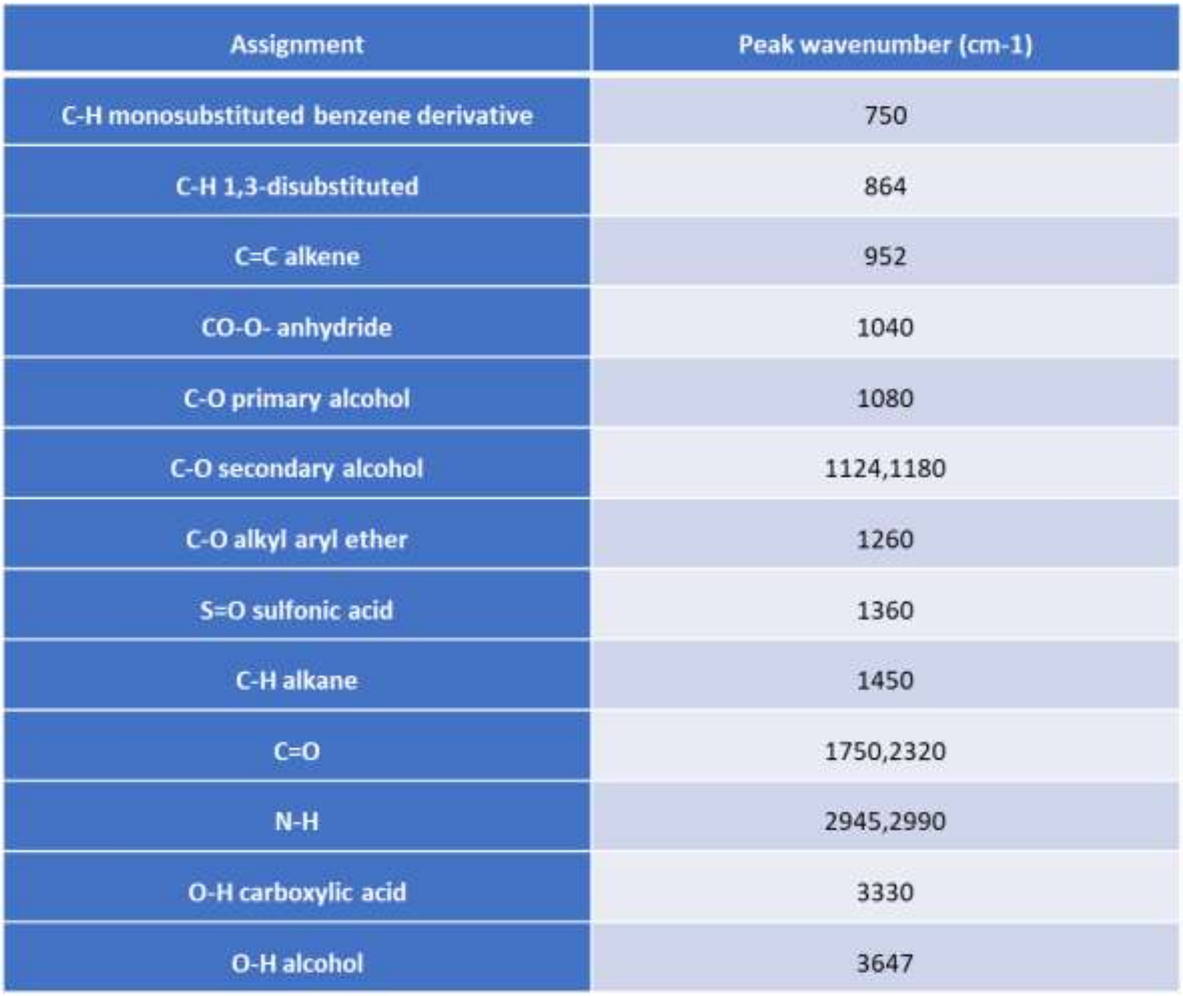
Figure 27. *Tensile strength, modulus and strain of composite based on wt% change*

Results discussion

FTIR

FTIR results of Lignin/PLA are shown in *Figure 16-18, 22-24.* The wavenumbers and important bands identifications of Lignin/PLA composites are shown in *Table 5.*

Table 6. *Bands assignments of Lignin/PLA composite results*



Assignment	Peak wavenumber (cm-1)
C-H monosubstituted benzene derivative	750
C-H 1,3-disubstituted	864
C=C alkene	952
CO-O- anhydride	1040
C-O primary alcohol	1080
C-O secondary alcohol	1124,1180
C-O alkyl aryl ether	1260
S=O sulfonic acid	1360
C-H alkane	1450
C=O	1750,2320
N-H	2945,2990
O-H carboxylic acid	3330
O-H alcohol	3647

Generally, the curves of Lignin/PLA show similar bands with increased emissivity compared to pure PLA. In *Figure16*, there are obvious peaks occurring at 3300 in L(10%) and L(15%) curves. In these two samples, the contents of pure lignin in the composites are highest, which means addition of lignin in the composites would lead to a higher content of hydroxy group. As it is discussed in **1.4 Acetylation**, if there are overmuch hydroxy groups in Lignin/PLA composites, it is hard to achieve a uniform distribution for the mixture because PLA is aliphatic polyester, thus, influences the mechanical property. Mechanical properties will be discussed later in this chapter.

To determine whether there is chemical reaction occurring in Lignin/PLA composite, a new curve with mathematic combination, which assumes there is no chemical reaction during producing composites, only physical combination occurs between PLA and lignin-based filler, was applied. An example about H(15%) is shown below.

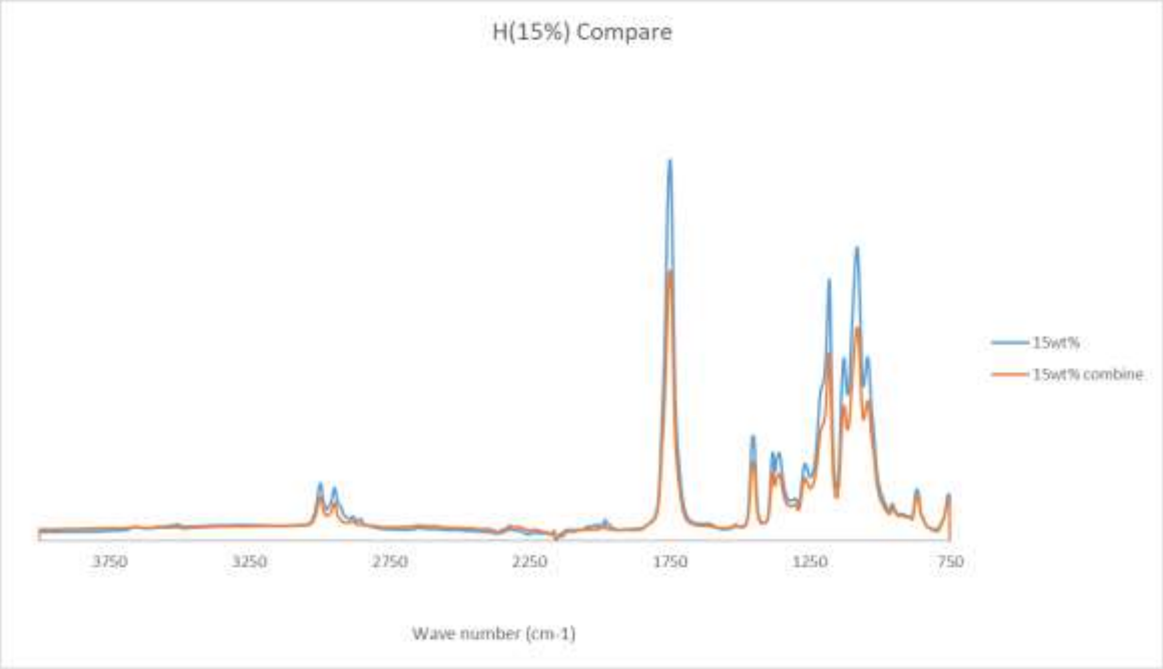


Figure 28. *Example of comparing original curve and calculated curve*

The emissivity of 15wt% combine curve is calculated by using the following equation:

$$Emissivity_{combine}=Emissivity_{PLA}*Concentration_{PLA} + Emissivity_{Lignin}*Concentration_{Lignin}$$

Weight percentage of lignin is based on weight of PLA, which means H(15%) composites contain 100% weight PLA and 15% weight Lignin. For instance, in this case, concentration of PLA is (100/115), and concentration of Lignin is (15/115).

Emissivity of wo curves is obviously different, original 7%Ash15 curve has a stronger emissivity. Same result can be collected in all other samples. Therefore, chemical reaction does generate between PLA and lignin during productive process of the composites.

TGA/DTG

In all TG charts in *Figure 19* and *Figure 25*, when weight percentage of lignin-based filler reaches 15wt%, the weight-loss-starting points in all three conditions occurs in advance compared to pure PLA curve. There is a limitation of lignin weight percentage in PLA, which is similar to that in PP [10]. The thermal property of Lignin/PLA composite with a higher weight percentage of lignin may contain more characteristic of thermal property of lignin. Based on the test results in ***Chapter 2.3.1***, the temperature that ADM lignin would start degradation is between 140^{o}C and 200^{o}C. Therefore, thermal property of Lignin/PLA composite is declined because weight percentage of lignin is too high that beyond the limitation.

The lignin used in this project is ADM lignin, which contains inorganic contents originally. In L lignin-based filler composites, only 15wt% curve shows a decline of weight-loss-starting temperature; in M lignin-based filler composites, both 10wt% and 15wt% show the decline, but 10wt% curve's change is not obvious; and in H lignin-based filler composites, decreasing trend occurs in all three curves. Inorganic content catalyzed the degradation of PLA, so that lignin-based filler with a relatively high ash content leads to a relatively low weight-loss-starting temperature. The process of washing lignin benefits in reducing inorganic content, thus, maintain the thermal stability of Lignin/PLA composites.

The maximum rate of change in mass is indicated by the peak in the DTG curves in *Figure 20* and *Figure 26*. In *Figure 20, b*y comparing with pure PLA, all samples, except H(10%) and H(15%), show an increase of the temperature, T_{max}, at which the peak (lowest point) occurs, which also means an increase of thermal stability. The only two exceptional samples contain the highest inorganic content, which could catalyze and accelerate the degradation of PLA. Furthermore, compared with pure PLA, the highest weight loss rates (lowest points) of all samples are declined, which could also indicate the inorganic content generates an accelerated degradation of PLA. In *Figure 26*, when the weight percentages of lignin-based filler are same, the peaks of 4%Ash samples are at the right end, which indicates the 4%Ash samples show more significant thermal stability than the samples with L lignin and H lignin. At the same time, the max mass loss rates of M lignin samples are higher than the rest.

As a conclusion, addition of lignin can increase the thermal stability of PLA only if the injected amount is not beyond the limitation. The cause of the influence on the thermal property of Lignin/PLA is a combination of both lignin and inorganic content. In **Chapter 2** of this project, M(5%) sample performs the best thermal stability.

Mechanical Properties

Tensile strength, modulus, and strain are tested as mechanical properties of Lignin/PLA composites by Discover Hybrid Rheometer (TA Instruments). The dimensions of samples for mechanical property test are 0.15 ± 0.05 mm in thickness, and 5 ± 1mm in width. Maximum force produced by the rheometer is 50N. All three properties can be tested at same time. Results are collected at the breaking point of the sample.

Figure 29. *Example of mechanical property test by DHR*

Results of mechanical properties are shown in *Figure 21* and *Figure 27*, which are about composites with same filler type and different filler contents and composites with different filler type and same filler contents, respectively.

In *Figure 21*, no matter which lignin was used as filler to produce Lignin/PLA composites, addition of lignin weight percentage would lead to a decline in tensile strength of the composites. Generally, all samples performed a decreasing tensile strength compared to pure PLA. Tensile strength of sample M(5%) was close to that of pure PLA, which is 48.39 MPa compared to 52.46 MPa. For L(15%) and H(15%) sample, current tensile strength is less than 40% of pure PLA, which is around 20 MPa. There is no trend in analysis about modulus of composites. Modulus of PLA increased with different level after injecting lignin-based filler. Toughness of PLA increased after being produced into Lignin/PLA composite, since all composites' strain has declined. Sample M(5%) has higher strain than other samples. Combined with the result of tensile strength, mechanical property of M(5%) sample is closest to that of pure PLA. In *Figure 27,* when the ash contents of lignin-based filler are same, M lignin samples always perform best in tensile strength and strain. The phenomenon indicates that ash with a controlled content in the lignin can benefit in preventing mechanical property of PLA from decreasing.

As there is a limitation in thermal property of Lignin/PLA composite that if weight percentage of lignin is beyond the limitation, thermal stability will decline. There seems another limitation in mechanical property as well. A weight percentage of ADM lignin which is higher than 5wt% could influence the mechanical property of PLA in a negative way.

Samples with highest and lowest tensile strength and strain are M(5%) and L(15%), respectively. FTIR curves of both samples are compared in *Figure 30.* The red curve, which indicates M(5%), shows higher peaks at where C-H, C=C, and C=O; in contrast, the green curve, which indicates L(15%), has a wider and higher peak at around 3300 cm^{-1}, which means more -OH groups exist. The result of this comparation verifies abundant amount of hydroxy group in Lignin/PLA composite leads to negative effect.

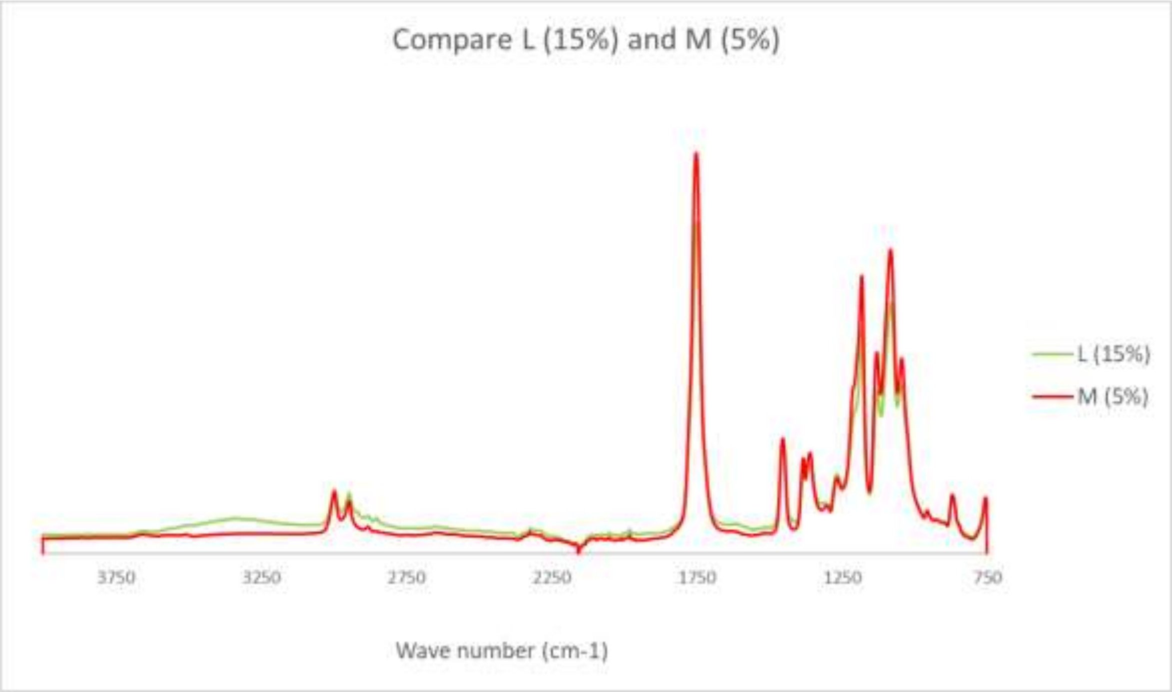


Figure 30. *Compare FTIR results of L(15%) and M(5%)*

Contact angle

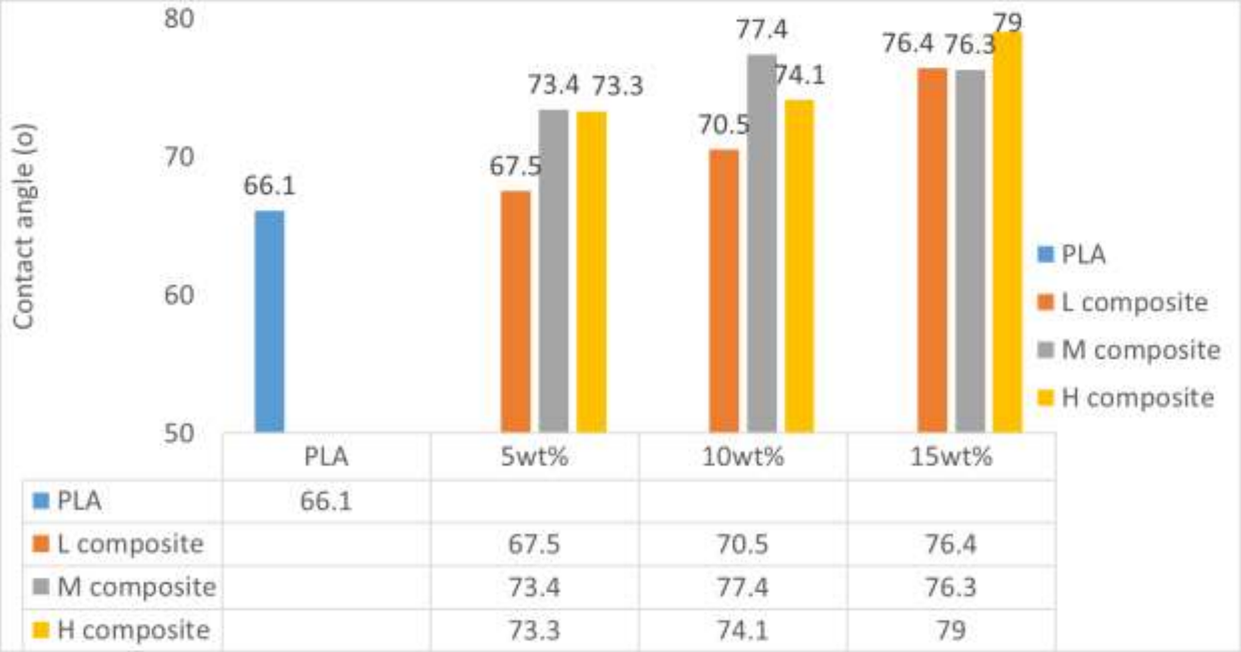
Contact angles of pure PLA, non-acetylated Lignin/PLA composites, and acetylated Lignin/PLA composites are measured, so that the changes in hydrophobicity of composites can be determined.

Contact angles of film samples are measured by directly dripping the deionized water onto the film surface. The thickness of the film is between 0.15mm and 0.25mm. The images are recorded by a high-speed camera (Fastcam Mini WX100, PCO) with a high 12x zoom lens system (LaVision). After 60 seconds, the contact angle is read by using a PFV software (Ver. 3670). The reported results are averages of at least 3 tests.

Figure 31. *Pictures of contact angle tests*

Pictures of contact angle measurements are shown in *Figure 31*, and numeric results are presented in *Table 7*.

Table 7. *Numeric results of contact angle tests*



	PLA	5wt%	10wt%	15wt%
■ PLA	66.1			
■ L composite		67.5	70.5	76.4
■ M composite		73.4	77.4	76.3
■ H composite		73.3	74.1	79

PLA shows contact angle values of 66.1^o on average. It can be concluded that contact angle increases after adding lignin into the composite, which obtains an improvement in hydrophobic character of PLA. Meanwhile, all Lignin/PLA composites, except M(10%), show same trend that additional filler content results a stronger hydrophobicity of composites. This trend is most obvious when ash content is low. As increase of inorganic ash content in lignin, the rising tendency slows down. The reason why M(10%) shows unconformable result could be the distribution of lignin-based filler in one of the tested samples is not uniform enough, which influences the hydrophobicity of testing point of the composite, thus, introduces an error in final average value of contact angle.

Morphology

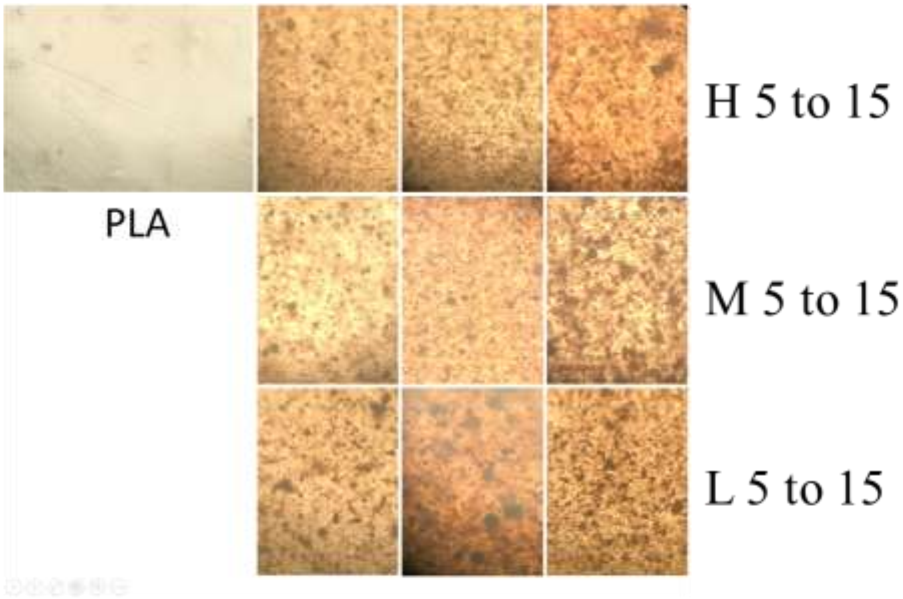


Figure 32. *Micrographs of composites*

Figure 32 shows micrographs of PLA and Lignin/PLA composites with different lignin fillers. It can be observed that all Lignin/PLA composites present aggregates. As filler weight percentages increase, more obvious particles can be seen in the micrographs. This could be due to incompatibility between PLA and lignin. [17]

Therefore, some conclusions can be made:

a) As it is mentioned, a ununiform distribution of filler in the composite can impair the mechanical properties. That's why mechanical properties of Lignin/PLA composites decline along as increasing lignin filler injected;

b) Composites with L lignin present higher OH groups in FTIR tests. Micrographs of L composites show more large-scaled particles in the composite. It is proved that hydroxyl group influences miscibility of lignin in PLA;

c) Compared with H and L composites, composites with M lignin fillers present better distribution of lignin in PLA, which makes tensile strength and strain of M composites are better than the others.

It is necessary to improve miscibility and distribution of lignin in PLA, so that mechanical properties of composites can be optimized.

CHAPTER 3. LIGNIN FILLERS IN PLA: THE EFFECTS OF ACETYLATION IN LIGNIN

3.1 Overview

As discussed in **1.4** Acetylation, hydroxy groups in lignin molecule can make it hard to achieve a uniform distribution for a Lignin/PLA mixture, thus, influences the mechanical property because PLA is aliphatic polyester. Introduction of acetyl groups will replace hydroxy groups by acetoxy groups during acetylation process. Lignin is acetylated to increase the affinity with biopolymers, such as PLA, and to prevent a deterioration of the mechanical properties. This conclusion is proved by results from **Chapter 2**: all composites made by untreated lignin and PLA showed a declined mechanical property compared to pure PLA. Since composites made by PLA and M lignin performed best mechanical and thermal properties, only M lignin is acetylated in this project to discover whether acetylation treatment can achieve an optimization or not.

In this chapter, acetylation is operated as a pre-treatment of lignin before producing Aced Lignin/PLA composites. Procedures of producing composites, including extrusion and heat press, and methods of testing, are same as the procedures in **Chapter 2**. Weight percentages of Aced M Lignin filler in PLA are fixed at 5wt%, 10wt%, and 15wt%. The details of acetylation procedures will be followed.

3.2 Experiment preparation

In **Chapter 3**, all experiment preparations are same to those in **Chapter 2**, except acetylation pretreatment is introduced.

Acetylation

Procedures from *Potential of producing carbon fiber from biorefinery corn stover lignin with high ash content* [14] for acetylation were applied for the first attempt. Acetic anhydride was mixed with lignin at 2.5mL*g^{-1} concentration (for instance, 5mL acetic anhydride + 2g M lignin). Mixture was kept in a beaker at 85^oC for 2 hours. Acetylated sample was subsequently heated at 140^oC for additional half an hour under vacuum ventilation. During the entire process, mixture was stirred at 150 rpm. After two stages, sample was stored in a widely opened container in vacuum oven for 48 to 72 hours until the acetylated lignin is totally dried.

The method provided in *Potential of producing carbon fiber from biorefinery corn stover lignin with high ash content* [14] was used to treat liquid precursors, which means acetylation was reacting in solution form. In this project, lignin is in powder form, which makes it difficult to be fully acetylated even excess acetic anhydride is applied. Based on FTIR result, hydroxy groups are removed obviously, but not thoroughly. Also, acetic acid is generated as a byproduct during acetylation process. After vacuuming dry, there is still distinctive sour taste and pungent smell in the sample.

To achieve a lower hydroxy group content and to eliminate byproduct after reaction, the method for acetylation is switched to the one according to *Lignin Acetylation* [15] provided by the University of Tennessee, Knoxville.

Dried M lignin was acetylated with acetic anhydride/pyridine (1/1, v/v) at room temperature for 24 hours. Concentrations for both acetic anhydride and pyridine were both 5mL*g^{-}1 (for instance, 1g M lignin + 5mL acetic anhydride + 5mL pyridine). Solution was stirred during the process at 100 rpm. After 24 hours, solvents were removed by a filter, during which lignin was washed with excess methanol and deionized water for three times to eliminate acetic acid. The precipitate was dried in vacuum oven at 40^{o}C for 24 hours before it was ready to produce Aced Lignin/PLA composite.

Figure 33 shows lignin before and after acetylation process. Color of lignin gets lighter because of reduction of the content of hydroxy group. [16]

Figure 33. *Left: M Lignin without acetylation; Right: Acetylation M Lignin*

3.3 Results and discussion

Testing results of acetylated lignin precursors and Aced Lignin/PLA composite will be discussed in this chapter. ThermoGravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), mechanical property tests are applied.

FTIR

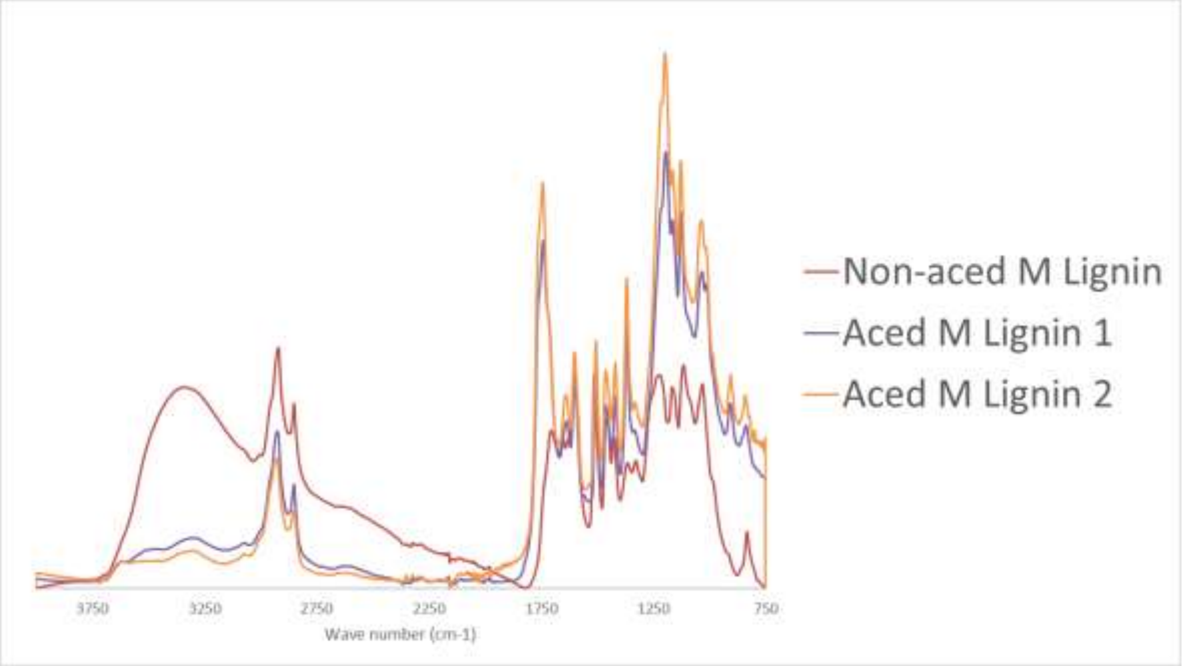


Figure 34. *FTIR results for Non-Aced M lignin, Aced M lignin in first attempt, and Aced M lignin in second attempt*

FTIR results for Non-Aced M lignin, Aced M lignin in first attempt, and Aced M lignin in second attempt are shown together in *Figure 34,* so that how acetylation process influences lignin molecule can be explained clearly.

In the case of Non-Aced M Lignin, a wide absorption band at 3300, which indicates the presence of hydroxy groups, can be observed. After acetylation treatment, content of hydroxy group is reduced obviously by comparing the strength of peaks at 3300.

Furthermore, the curve of Aced M Lignin 2 has a weaker peak at 3300 than the curve of Aced M Lignin, which indicates that the new method of acetylation makes a progress in eliminating OH groups. Thus, a more uniform distribution of Aced M Lignin in PLA becomes possible, which leads to a better mechanical property. Obviously increased peaks at 1040, which corresponds CO-O of anhydride, and at 1750, which corresponds C=O of ester, (*Table 6*) is introduced during acetylation process. This indicates that the acetylation process is successful. [12]

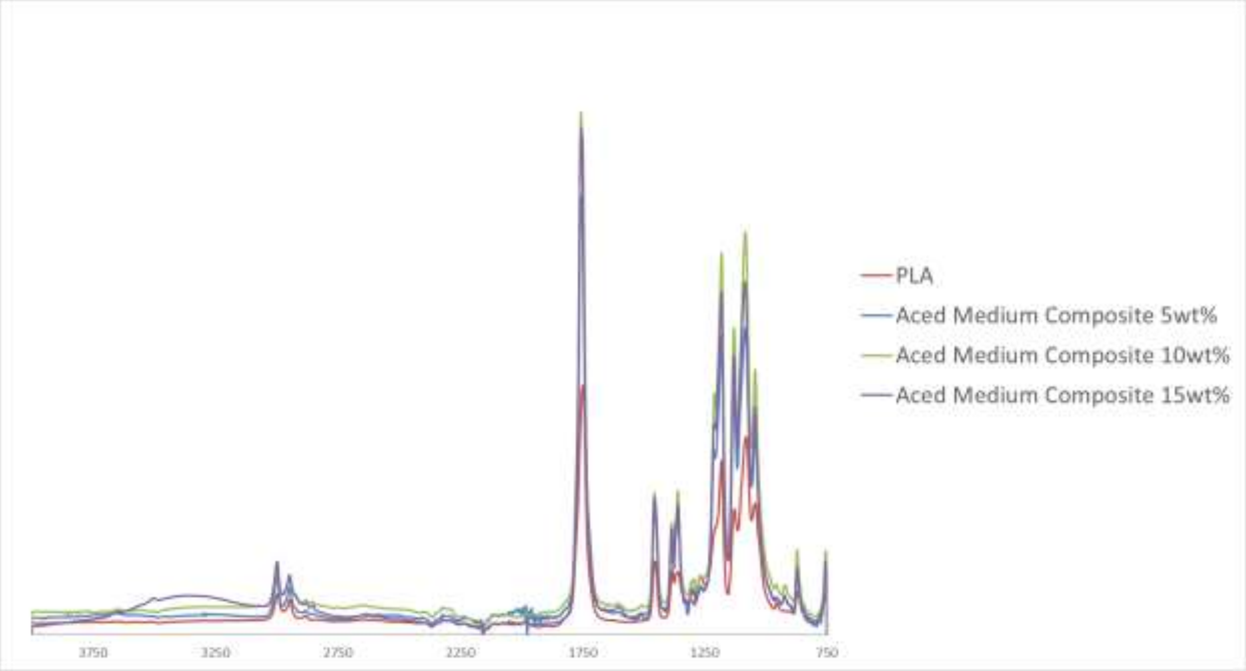


Figure 35. *FTIR results for Aced M Lignin/PLA composites with different wt%*

FTIR results for Aced M Lignin/PLA composites with different wt% are shown in *Figure 35.* Along as the increase of weight percentage of Aced M Lignin filler in the composites, content of hydroxy group increases as well. In *Figure 34,* the curves of Aced M

Lignin at 3300 are not flat, which means acetylation process can reduce hydroxy group content, but cannot completely remove all OH groups. Additional Aced M Lignin filler introduces more OH groups into composites unavoidably.

TGA/DTG

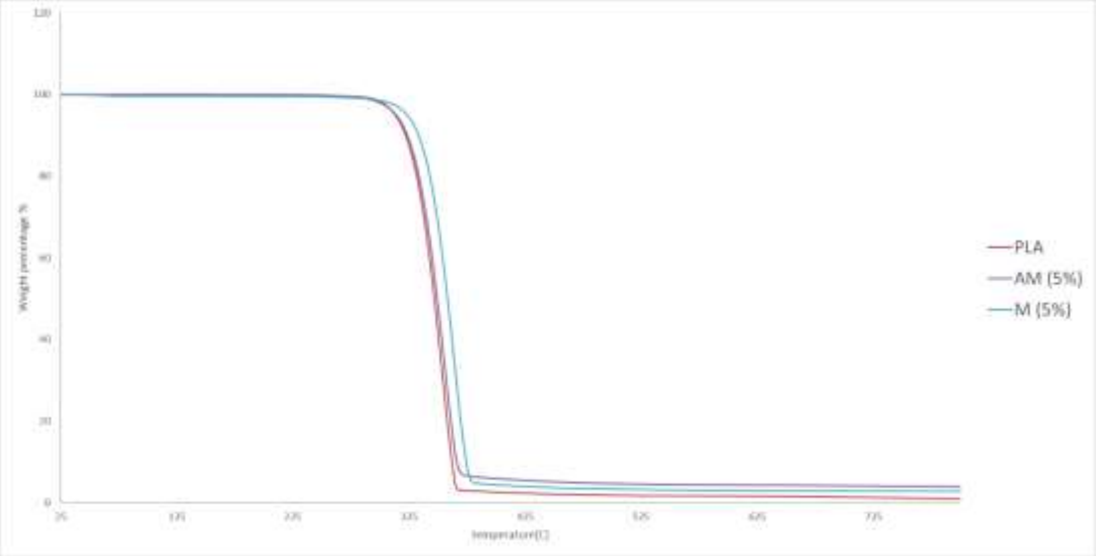


Figure 36. *TGA results of comparison among AM(5%), M(5%), and PLA*

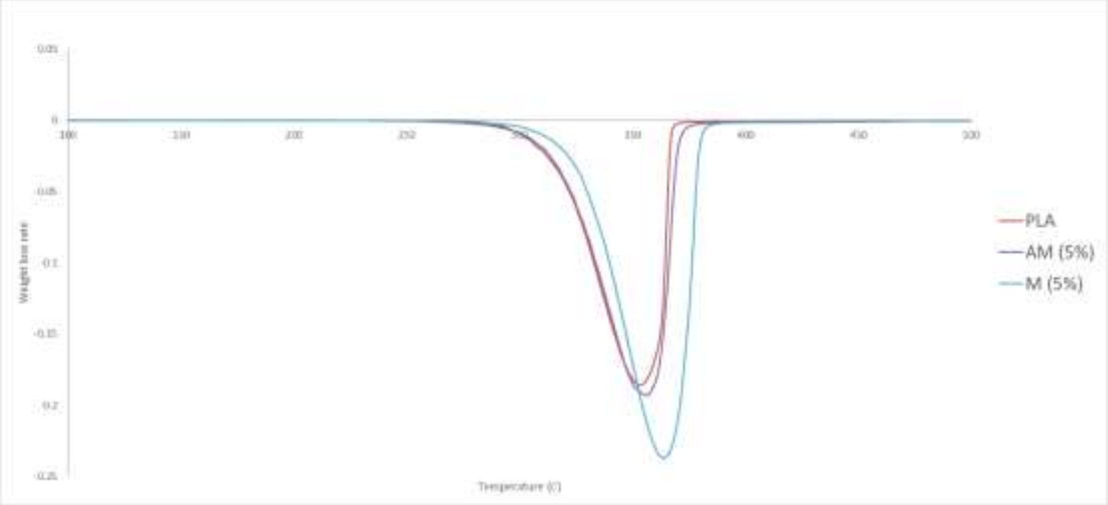
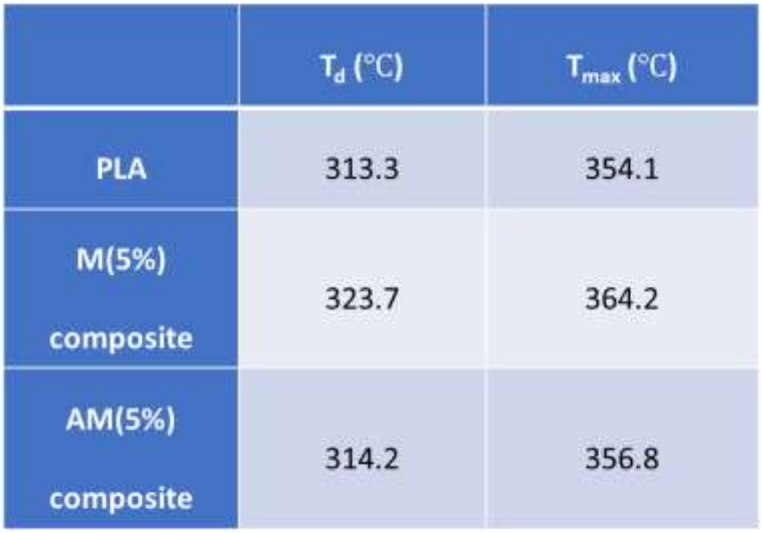


Figure 37. *DTG results of comparison among AM(5%), M(5%), and PLA*

TGA and DTG results of comparison among AM(5%), M(5%), and PLA are shown in *Figure 36* and *Figure 37*, respectively. T_d, the temperatures at which 5% weight losses occur, and T_{max}, the temperatures at which the maximum weight loss rate occur, of PLA, composite with 5wt% of non-aced M lignin filler, and composite with 5wt% of acetylated M lignin filler are shown in *Table 8*.

Table 8. *T_d and T_{max} comparison*



	T_d (°C)	T_{max} (°C)
PLA	313.3	354.1
M(5%) composite	323.7	364.2
AM(5%) composite	314.2	356.8

M(5%) performed best mechanical and thermal properties in **Chapter 2**. After acetylation treatment, AM(5%) show decline in both T_d and T_{max}, which means this chemical pretreatment on filler reduced the thermal stability of Lignin/PLA composites. However, T_d and T_{max} of the AM(5%) composite are still higher than pure PLA. Combining the results of TGA/DTG in both **Chapter 2** and **3**, it confirms that adding filler into PLA can improve thermal stability. Further study about whether additional CO-O- and C=O groups after acetylation could be the reason why T_d and T_{max} decreased can be employed.

Mechanical Properties

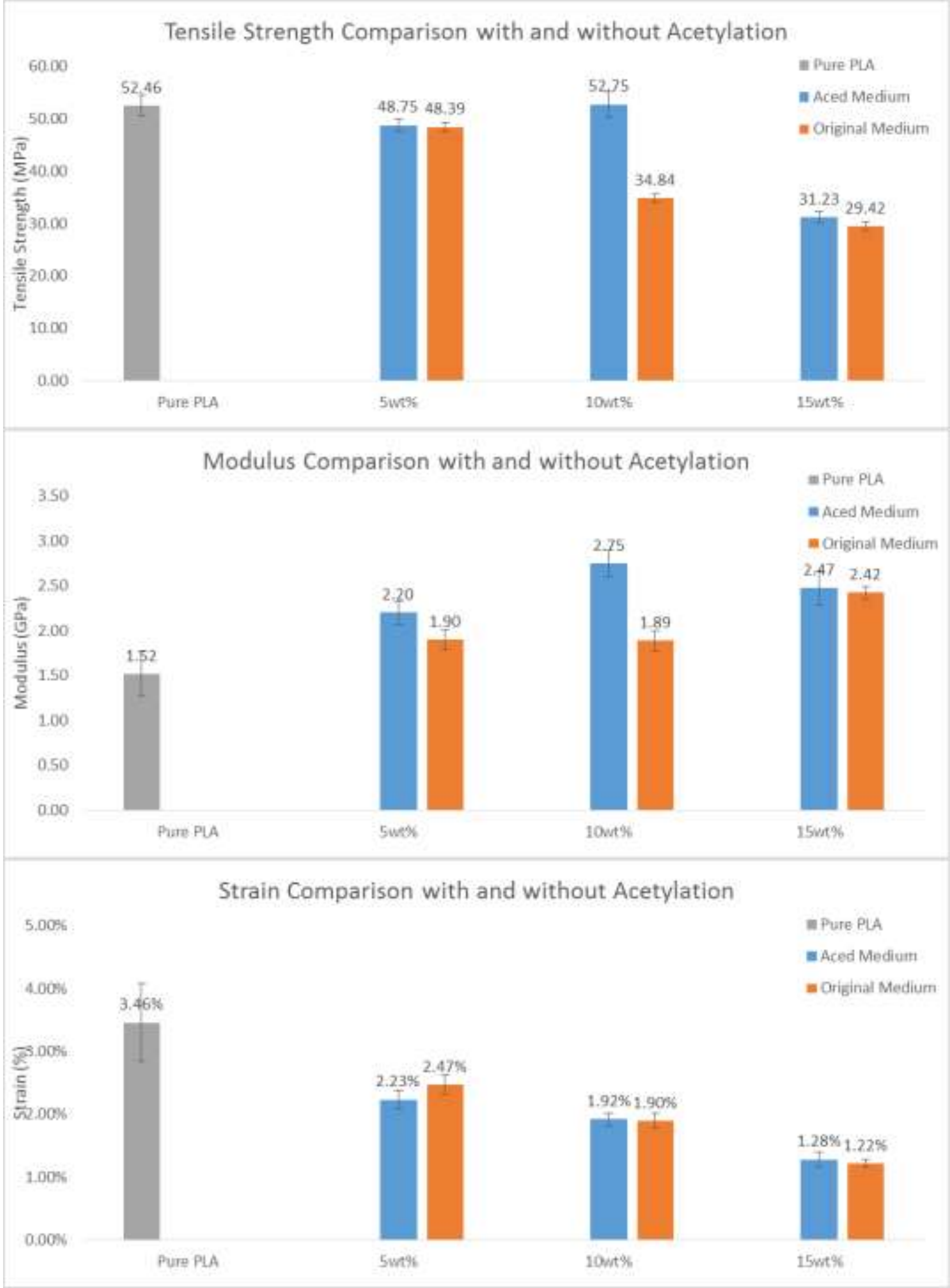


Figure 38. *Tensile strength, Modulus, and strain Comparison between Aced and Non-aced M composites*

Results of mechanical properties test are shown in *Figure 38*. For AM(5%) and AM(15%) samples, values of tensile strength are close to M(5%) and M(15%), respectively. Acetylation treatment doesn't improve at these two weight percentage level. However, when weight percentage is 10wt%, acetylation plays a driving role in improving tensile strength, which is increased from 34.84 MPa to 52.75 MPa. Tensile strength of AM(10%) is roughly equal to that of pure PLA. Therefore, at a lower weight percentage level of filler (lower than 15wt%), acetylation does help to prevent tensile strength decreasing along as weight percentage increasing. Generally, acetylated lignin filler can certainly improve modulus of Lignin/PLA composites, like non-acetylated lignin filler, both exert a positive influence. This effect seems to stop until weight percentage reaches 15wt%. At 10wt%, increase of modulus attains maximum. While, the result does not show that acetylation is able to improve strain of the composites. Strains of both acetylated and non-acetylated samples are quite similar: additional filler makes the strain of the composites decreased.

Based on the results shown above, it can be concluded that at a lower weight percentage (5wt% and 10wt%), injecting acetylated lignin filler into PLA can maintain the tensile strength, meanwhile, increase modulus. Even there is a loss of strain, acetylated lignin filler does improve more mechanical property of Lignin/PLA composites.

Pure PLA film and samples (AM10% and M5%) with best performance in mechanical property test and thermal stability test from Chapter 2 and 3 are stored in a furnace at 40°C. Mechanical properties are tested again after 48 hours and 72 hours to determine whether injecting lignin-based filler can influence storage ability of PLA or not. Mechanical properties tests results are shown in *Figure 39.*

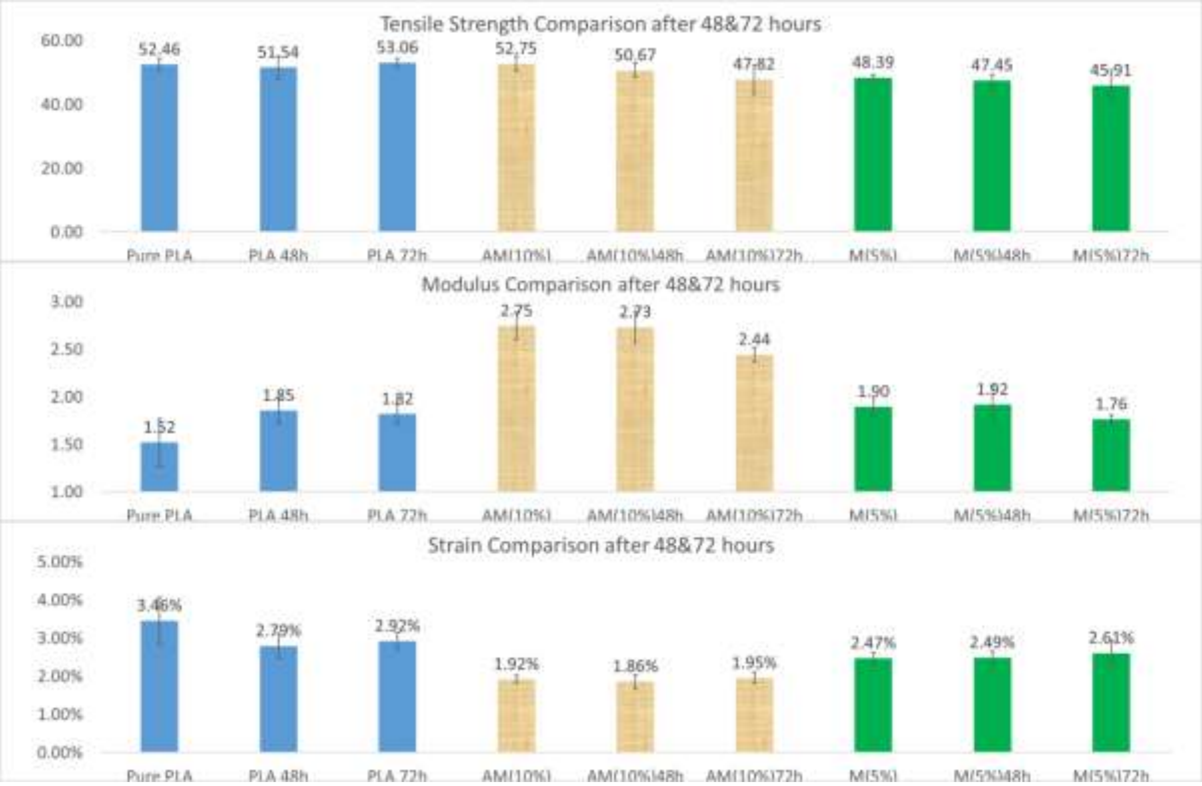


Figure 39. *Mechanical property results after 48h and 72h at 40°C*

For pure PLA, tensile strength shows steady after 72 hours' heat treatment, meanwhile, modulus starts to rise, and strain starts to reduce after 48 hours, which means PLA performs a weaker ductility. For composites samples with either acetylated or non-acetylated lignin filler, tensile strength keeps slightly decreasing with additional time, which can be noticed after 48 hours. In contrast, modulus for both samples shows no obvious change until they are heat-treated 72 hours, and strain keeps stable through the entire experiment. The results indicate that lignin filler (aced or non-aced) can delay PLA to become fragile in an above-room-temperature atmosphere, even the tensile strength of the composite will reduce slightly. Lignin-based filler plays the role in maintaining ductility of PLA.

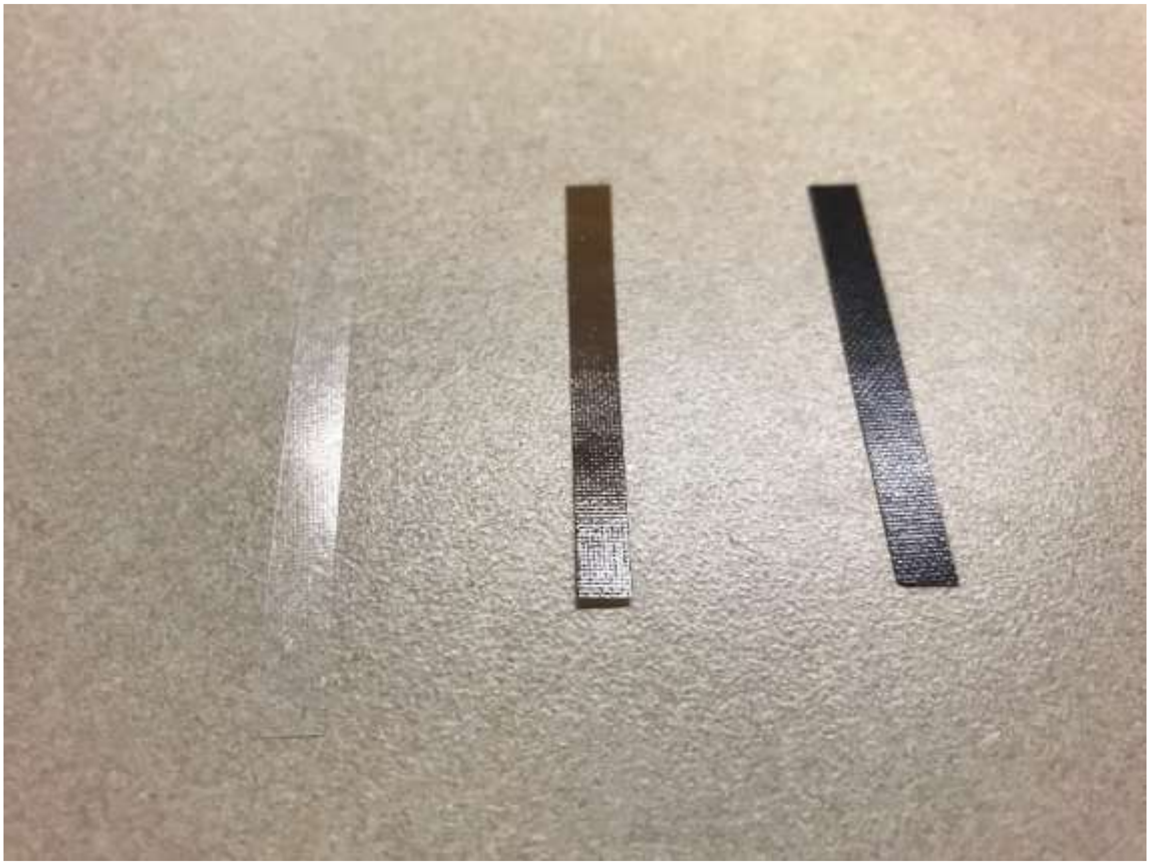


Figure 40. *Left: PLA film; mid: AM(10%) film; right: M(5%) film*

Contact angle

In **Chapter 3**, contact angles of acetylated Lignin/PLA composites are determined by the same method as that in **Chapter 2**.

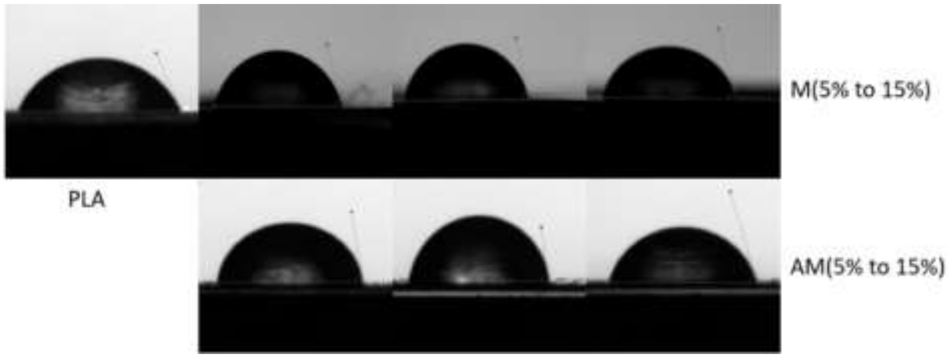


Figure 41. *Pictures of contact angle tests (2)*

Pictures of contact angle measurements are shown in *Figure 41*, and numeric results' comparison between acetylated Lignin/PLA and non-acetylated Lignin/PLA composites are presented in *Table 9*.

Table 9. *Numeric results of contact angle tests (2)*

	PLA	5wt%	10wt%	15wt%
🟧 PLA	66.1			
🟦 M composite		73.4	77.4	76.3
🟨 AM composite		81.7	81.3	75.4

Since acetylation can substitute hydroxyl groups with $COCH_3$- groups, which are non-polar function groups, hydrophobic character of lignin can be improved, thus, contact angle of Lignin/PLA composites will be enlarged. [3] The results shown in *Table 9* proves the theory. After acetylation, AM composites present higher hydrophobicity than original M composites, the effect reaches maximum since weight percentage is 5wt%. However, the value of contact angle starts to decrease until weight percentage of filler reaches 15wt%, which could be due to increased roughness of the samples. Similar to the conclusion of mechanical property test, there should be an optimum filler content, beyond which additional acetylated filler will start to decrease hydrophobicity of composite.

Morphology

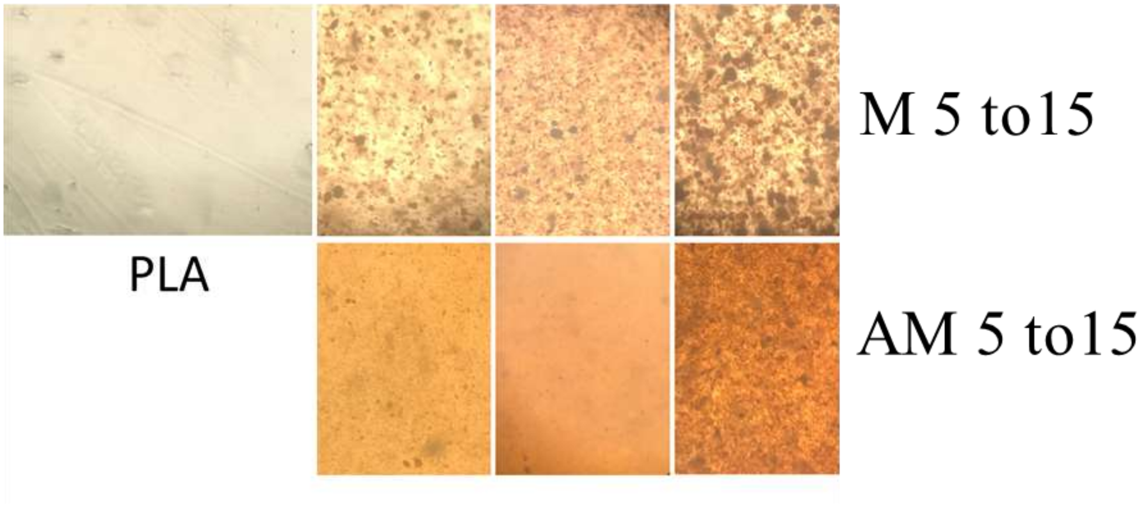


Figure 42. *Micrographs of composites (2)*

Figure 42 shows morphology test results of acetylated M Lignin/PLA composite, and compared with pure PLA and non-acetylated M Lignin/PLA composites. It is obvious that acetylation treatment fortifies miscibility of lignin in PLA. At 5wt% and 10wt%, particles in composites are eliminated so much, especially in AM(10%) composites, which perform best in tensile strength and modulus tests. Also, the graphs of AM composites present more uniform colors, unlike M composites, in which the original color(ivory) of PLA can still be told. The change of colors proves that acetylation increases miscibility of lignin in PLA, thus, mechanical properties of composites are improved. However, obvious particles are shown in AM(15%) composite, of which mechanical properties are close to those of non-acetylated M(15%). The phenomenon verifies that there is also an optimum filler content, beyond which an adverse effect on filler miscibility and distribution will occur.

CHAPTER 4. CONCLUSIONS

In this project, it is successful to determine mechanical and thermal properties of Lignin/PLA composites, in which the lignin-based filler is produced by corn stover lignin. Inorganic ash contents are controlled at 7%, 4%, and 2% by adjusting acid wash degree. Lignin filler in PLA does reduce the tensile strength and strain, whereas tensile modulus and thermal stability of the composites are increased. However, inorganic ash in lignin cannot be ignored, since high ash content in lignin filler can reduce both thermal stability and mechanical properties of Lignin/PLA composites. According to the results shown in **Chapter 2**, it seems that there is an optimum ash content in lignin, which is 4% in this project. The combined effect of lignin and inorganics is helpful in maximize the mechanical and thermal properties. After the study of non-pretreated lignin filler, acetylation is applied as chemical pretreatment to remove hydroxy groups in lignin, so that the distribution of lignin-based filler in PLA can be more uniform. Acetylation in this project is successful, based on FTIR results, and effects an increased modulus of Lignin/PLA composites without reducing tensile strength (up to 10wt%). Results in **Chapter 3** also show that adding lignin-based filler (acetylated or non-acetylated) delays strain loss of PLA in above-room-temperature atmosphere. Meanwhile, hydrophobicity of PLA is increased by injecting lignin-based fillers (acetylated and non-acetylated).

CHAPTER 5. FUTURE STUDY AND RECOMMENDATIONS

(1) Inorganic ash content of ADM lignin can be controlled at more different levels to determine a more accurate one, with which the filler can help in maximizing the properties of Lignin/PLA composites;

(2) Further study of which exact kind of inorganic ash can influence the properties positively is necessary;

(3) Procedures of producing Lignin/PLA composites film can be optimized to achieve a more uniform distribution of filler in composites;

(4) Process of acetylation could be optimized, so that the cost and treating time can be reduced;

(5) Lignin/PLA composites films can be stored in oven with extended time, which will help in providing more details about composites degradation;

(6) Hydrophobicity of composites needs be improved;

(7) A third agent can be added to the composite to improve tensile strength.

REFERENCES

[1] Lignin. (2017, October 01). Retrieved October 05, 2017, from https://en.wikipedia.org/wiki/Lignin

[2] Gordobil, O., Delucis, R., Egüés, I., & Labidi, J. (2015). Kraft lignin as filler in PLA to improve ductility and thermal properties. Industrial Crops and Products, 72, 46-53. doi: 10.1016/j.indcrop.2015.01.055

[3] Gordobil, O., Delucis, R., Egüés, I., & Labidi, J. (2015). Kraft lignin as filler in PLA to improve ductility and thermal properties. Industrial Crops and Products, 72, 46-53. doi:10.1016/j.indcrop.2015.01.055

[4] Departement of Chemical and Biological Engineering, Chalmers University of Technology Follow. (2013, July 09). Lignin biomass recalcitrane. Retrieved October 06, 2017, from https://www.slideshare.net/isroi/lignin-biomass-recalcitrane

[5] Lunt, J. (1998). Large-scale production, properties and commercial applications of polylactic acid polymers. Polymer Degradation and Stability, 59(1-3), 145-152. doi:10.1016/s0141-3910(97)00148-1

[6] Vink, E. T., Rábago, K. R., Glassner, D. A., & Gruber, P. R. (2003). Applications of life cycle assessment to NatureWorks™ polylactide (PLA) production. Polymer Degradation and Stability, 80(3), 403-419. doi:10.1016/s0141-3910(02)00372-5

[7] David E. Henton, Patrick Gruber, Jim Lunt, and Jed Randall. (n.d.). Retrieved October 7, 2017, from http://www.bing.com/cr?IG=3411B64EAC34475094D3F600D65DCA1E&CID=2E410B99856561690E41008D84636067&rd=1&h=82mzshQU0mUYtuT4uOy4tF6GiuIDR83ABQakvQxf-Xk&v=1&r=http%3a%2f%2fwww.jimluntllc.com%2fpdfs%2fpolylactic_acid_technology.pdf&p=DevEx,5062.1

[8] Rogers, T. (n.d.). Creative Mechanisms Blog . Retrieved October 07, 2017, from https://www.creativemechanisms.com/blog/learn-about-polylactic-acid-pla-prototypes

[9] Jamshidian, M., Tehrany, E. A., Imran, M., Jacquot, M., & Desobry, S. (2010, August 26). Poly-Lactic Acid: Production, Applications, Nanocomposites, and Release Studies. Retrieved October 08, 2017, from http://onlinelibrary.wiley.com/doi/10.1111/j.1541-

4337.2010.00126.x/full

[10] Toriz, G., Denes, F., & Young, R. A. (2004, April 15). Lignin-polypropylene composites. Part 1: Composites from unmodified lignin and polypropylene. Retrieved October 09, 2017, from http://onlinelibrary.wiley.com/doi/10.1002/pc.10478/abstract

[11] Comparison of the thermal, dynamic mechanical and morphological properties of PLA-Lignin & PLA-Tannin particulate green composites. (2015, August 20). Retrieved October 10, 2017, from http://www.sciencedirect.com/science/article/pii/S1359836815004588

[12] Gordobil, O., Egues, I., Llana-Ponte, R., & Labidi, J. (2014). Polymer Degradation and Stability. Retrieved October 10, 2017, from https://www.journals.elsevier.com/polymer-degradation-and-stability/

[13] Xue, Y., Zhou, S., & Bai, X. (2016). Role of Hydrogen Transfer during Catalytic Copyrolysis of Lignin and Tetralin over HZSM-5 and HY Zeolite Catalysts. ACS Sustainable Chemistry & Engineering, 4(8), 4237-4250. doi:10.1021/acssuschemeng.6b00733

[14] Qu, W., Liu, J., Xue, Y., Wang, X., & Bai, X. (2017). Potential of producing carbon fiber from biorefinery corn stover lignin with high ash content. Journal of Applied Polymer Science, 135(4), 45736. doi:10.1002/app.45736

[15] Lignin Acetylation. (n.d.). Retrieved from http://biorefinery.utk.edu/technical_reviews/Lignin%20Acetylation.pdf

[16] STABILIZATION OF WOOD COLOR: IS ACETYLATION BLOCKING ... (n.d.). Retrieved November 3, 2017, from https://www.bing.com/cr?IG=D8A08029D1F54078A7C369FF6381810F&CID=043D4D0B6E7562111B3F46246F736343&rd=1&h=0mraYRWnUPmxYXtdpofk7aQ0lxgwzDr3pi1uFavFkJs&v=1&r=https%3a%2f%2fwfs.swst.org%2findex.php%2fwfs%2farticle%2fdownload%2f1302%2f1302&p=DevEx,5064.1

[17] Polymer Degradation and Stability. (n.d.). Retrieved November 06, 2017, from https://www.journals.elsevier.com/polymer-degradation-and-stability

.