

PREPARATION and CHARACTERIZATION of GREEN COMPOSITE USING BIOMIMETIC MODIFIED LIGNIN

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Abstract

In this study, two types of alkyl-chain-based modification agents were used. The two alkyl chain derivatives block the hydroxyl groups of lignin and replace them with glycoside. Cellulose is compatible with hemicellulose, which is coupled to lignin by ether, glycoside and ester bonds in plant fibers. To mimic this structure, in this study, lignin was combined with an alkyl chain with a similar SP value and was used as a matrix polymer to form glycoside bonds. PLA-modified lignin (PLAL) and tetrahydrofuran-modified lignin (THFL) exhibited remarkable changes in the presence of an alcohol functional group. The results of 1-H NMR analysis confirm those obtained by FT-IR analysis. The results of the DSC analyses indicate that lignin and modified lignin exhibit different thermal properties. The results of the thermal and mechanical analyses of the modified lignin/PLA blends demonstrate that the characteristics of the alkyl chains used to modify lignin were well reflected in the final blends.

1. Introduction

Lignin has enormous potential as a raw material for polymer industries. But, lignin has not been utilized well as a raw material because of its brittleness and difficulty to be processed. Therefore, chemical modification of lignin is a big issue of the lignin research area. Main idea of chemical modification is to replace the carboxyl group or hydroxyl group of lignin by alkylation, acylation and hydroxyalkylation.

The theoretical basis is based on the fact that lignin exists in the form of lignin carbohydrate complex(LCC) in plants. To mimic this structure, in this study, lignin was combined with an alkyl chain with a similar SP value and was used as a matrix polymer to form glycoside bonds. In this study, two types of reagents are used, and the reagents are chemically bonded with lignin to mimic the LCC structure. Non-modified lignin has an amphiphilic nature because of the hydrophilic hydroxyl groups and the hydrophobic benzene ring. In the case of the polymeric materials blend, polymers are blended well so that the polymer solubility parameter(SP) values are close to each other. This is similar to the well-mixed combination of water and alcohol. Proto lignin forms a covalent bond with hemicellulose chemically via a ester bond or ether bond in plants. And the reagents are chemically bonded with lignin to mimic that LCC structure. This relationship between lignin and the alkyl chain is similar to that between the Xylan and lignin. (Fig. 1.)

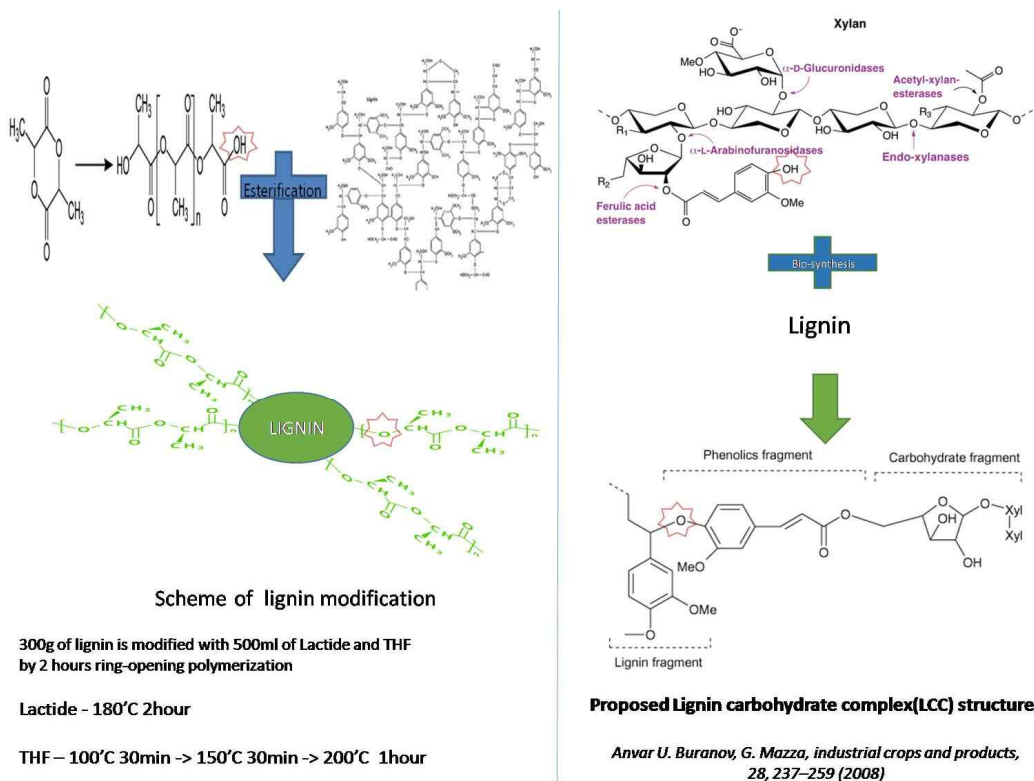


Figure 1. Scheme of lignin modification

2. Experimental

Materials and Methods

Oligomerized-(lactic acid) is prepared for Poly Lactic Acid modified lignin(PLAL). 1wt% Lactic acid is used as a chemical modification catalyst. In order to prepare tetrahydrofuran modified lignin(THFL), lignin is modified with 1 wt% sulfuric acid as catalyst. Lignin is purchased from MeadWestVaco, Indullin AT, SKL. Lignin reacted with PLA and THF by 2hours heating and stirring. (Fig. 2.)

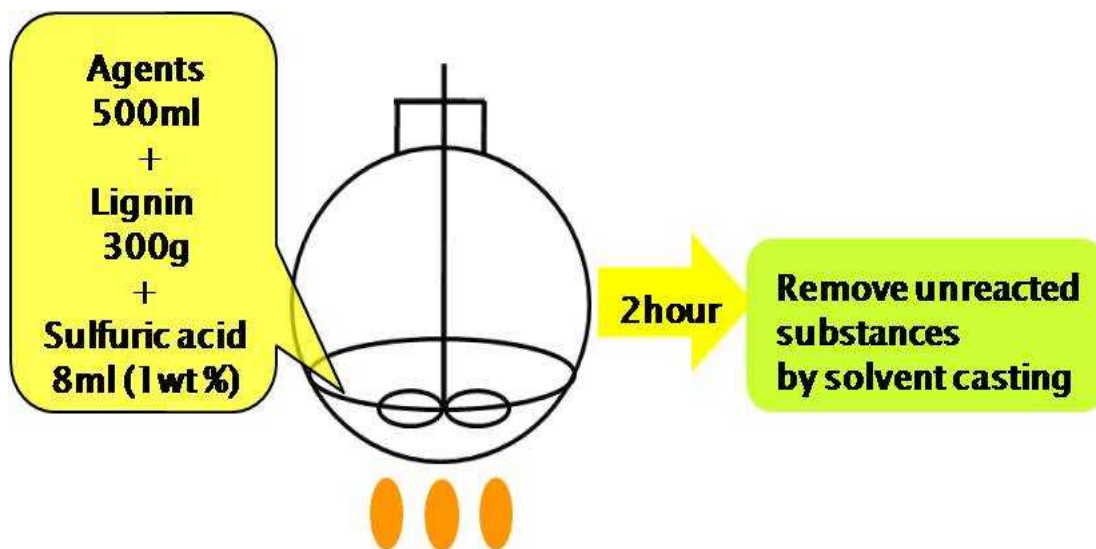


Figure 2. Process of lignin modification

Chemically modified lignin is blended with Poly Lactic Acid(PLA)(T_g - 65°C, M_w - 80,000) as the matrix. Modified lignin is as mixed with PLA in proportions ranging from 0 to 60.0 wt% at intervals of 20 wt% (0, 20, 40 and 60.0 wt%). The mixtures are melt-blended using a table-type kneader (PBV-0.3, Irie Shokai Co., Japan) at 150±2°C for 20 minutes. Subsequently, the modified lignin/PLA blends are compression molded using a two-post manual hydraulic press (#2699, Carver Inc., USA) at 150±1°C and 6.89 MPa for 5 minutes. The molds are quenched after molding, and polymer composite sheets are obtained.

Characterization

FT-IR

To investigate the chemical properties of lignin and modified lignin, solid-state FTIR spectra for the samples are obtained by FTIR spectrophotometer (Nicolet 6700, Thermo Scientific Inc., USA) using ATR (attenuated total reflectance) technique.

¹H-NMR

To investigate the chemical properties of the lignin and modified lignin, ¹H-NMR spectra of the samples were obtained using a 400 MHz NMR spectrometer (JeolJNM-LA400 with LFG, JEOL, JAPAN).

Thermal Properties

A differential scanning calorimeter (DSC-Q1000, TA Instrument Inc., UK) is used to investigate the thermal transition behavior of modified lignin and modified lignin/PLA blends.

Mechanical Properties

A universal testing machine (LRXPlus, LLOYD Instruments Inc., UK) is used to investigate the tensile properties of the modified lignin/PLA blends.

3. Results and discussion

FT-IR

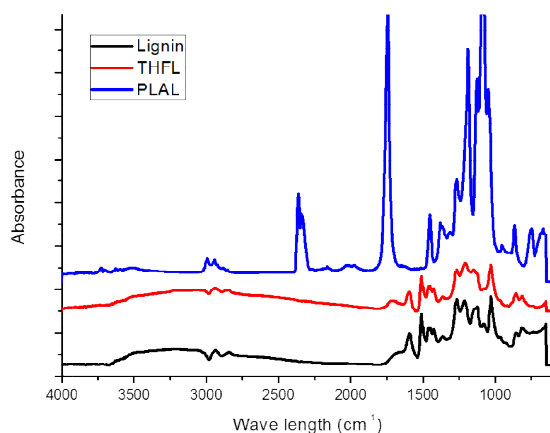


Figure 3. FT-IR spectra of lignin and modified lignin

FT-IR spectra of PLAL shows very strong peak at 1168cm^{-1} (C-O peak) and at 1747cm^{-1} (C=O peak) while spectra of pure lignin shows weak signal at those wavelengths. FT-IR spectra of THFL shows the reduced peak at 3250cm^{-1} (OH peak). This indicates that the hydroxyl groups of lignin are well replaced with alkyl chains by the modification.(Fig. 3.)

1H-NMR

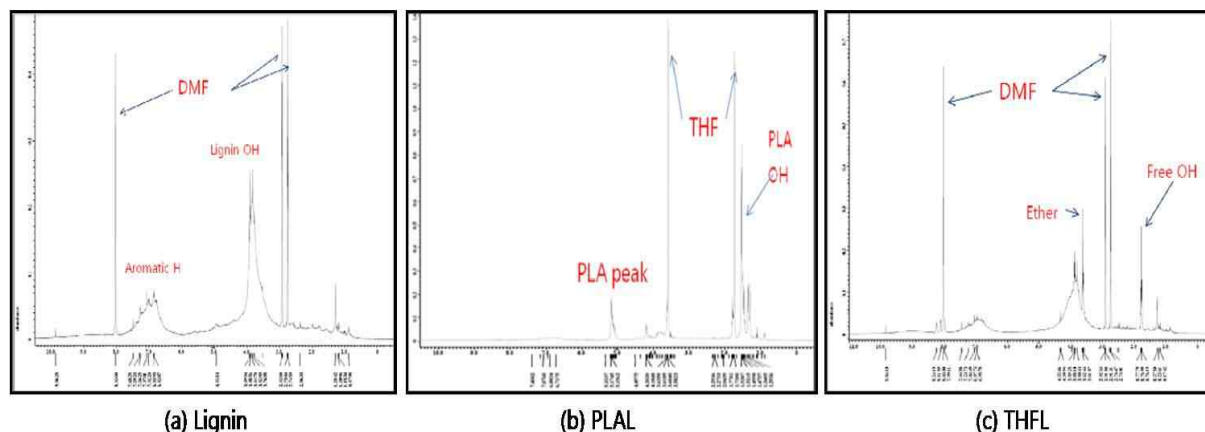


Figure 4. 1H-NMR analysis of lignin and modified lignin

As shown in Figure 4, the aromatic OH(ArOH) and aliphatic OH(AIOH) of lignin are reduced significantly in both PLAL and THFL. This indicates that as the result of the FT-IR, lignin is substituted with an alkyl chain by modification agents. Furthermore, the alkyl chain that replaces the hydroxyl group of the lignin reduced the brittle nature of the lignin. THFL shows low block yield (37.2 %) and has more remaining ArOH (9.86 ppm) and AIOH (3.88 ppm) compared with that of PLAL. PLAL is modified by the alkyl chain and shows high yield of block OH(91 %).(Table 1.) Furthermore, modification is confirmed by the presence of the specific PLA signal near 5.0 ppm.

	ArOH	AIOH	OH Block Yield
Lignin	0.026	0.36	0%
PLAL	0.002	0.04	91%
THFL	0.02	0.175	37.2%

Table 1. Yield of the lignin OH block by 1-H NMR analysis

Although almost the same amount reagent was used and the modification yields showed little difference (41.5 wt% vs. 31.7wt%), the yield of block OH and terminal hydroxyl group (free OH)of the alkyl chain showed large differences. This indicates that PLAL has multiple short chain and THFL has a long chain. It can also be confirmed by DSC analysis of the lignin and modified lignin.

Furthermore, it was confirmed by Sun et al. In a study of the hydroxyalkylation of lignin to use as polyols. This shows that, with high catalyst contents, hydroxyalkylated lignin became multiple short chain grafted and most of the lignin hydroxyl group reacted, whereas the low catalyst contents condition is diametrically opposed.

Thermal Properties of Lignin and Modified Lignin

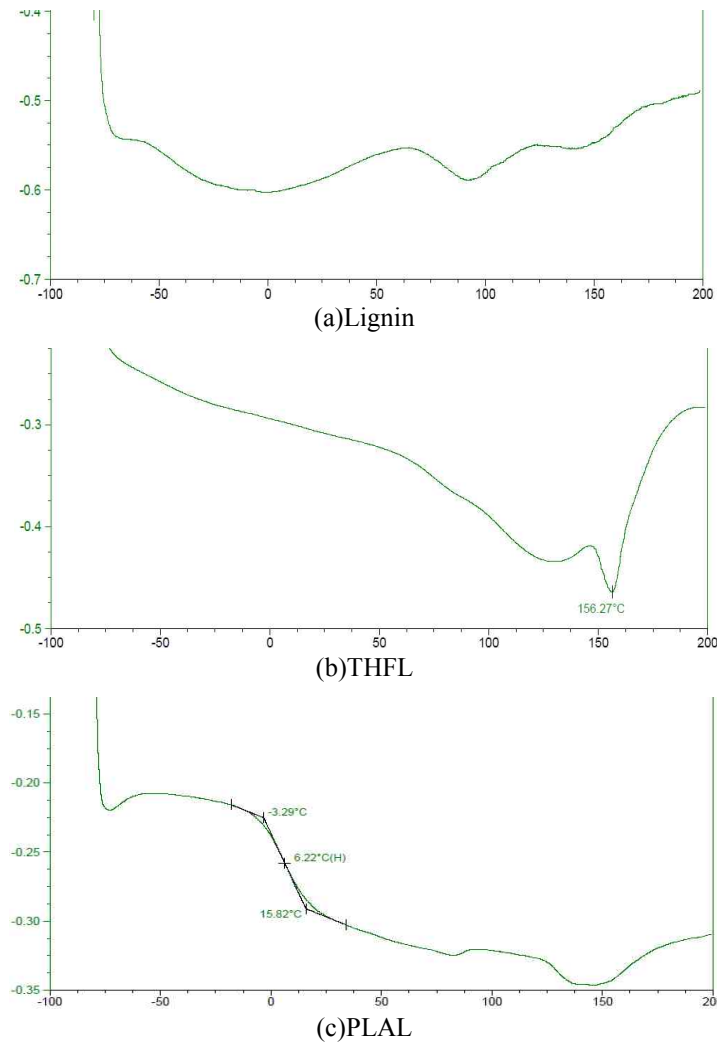


Figure 5. DSC analysis of lignin and modified lignin

Lignin has a characteristic nature called 'sintering' and became a thermosetting polymer at approximately 160 ~ 200°C through irregular bonding between its own functional groups. Therefore, lignin shows no specific Tg or Tm. However, the thermal properties of lignin were changed by the alkyl chain substitution of the hydroxyl group of lignin. It can be shown that PLAL has a Tg, and THFL has a Tm. These peaks are due to the peaks of the alkyl chain. In the case of PLAL, the Tg is at 6.22°C. (Fig. 5.)

It is caused by the low molecular weight PLA used in the modification. As described above, PLAL has multiple short chains, and THFL has a small, long chain. Therefore, the alkyl chain of PLAL is too short to form a lamella structure; it has no Tm. Meanwhile, the alkyl chain of THFL packed densely and shows no specific Tg.

These phenomenon are the cause of the PLAL/PLA blend showing low mechanical properties. As described above, the low molecular PLA alkyl chain has a low Tg. These low Tg chains work as defects in the matrix - PLA has a 65°C Tg. This can be confirmed by A. J. Nijenhuis et al.

Thermal Properties of Blend

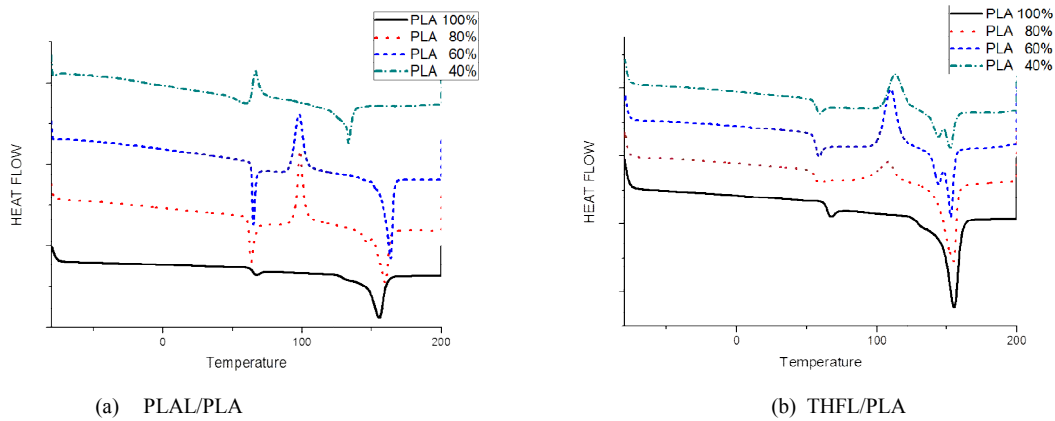


Figure 6. DSC analysis of modified lignin/PLA blend

The DSC analysis shows that phase change of modified lignin and PLA with different blend ratio. (Fig. 6.) However, when the ratio of PLA blends with different modified lignin, it can be found that the addition of modified lignin, the thermal properties of PLA is changed. Furthermore, it is observed that the thermal and physicochemical properties of modified lignin/PLA blend could be adjusted according to the characteristics of the alkyl chains.

Mechanical properties

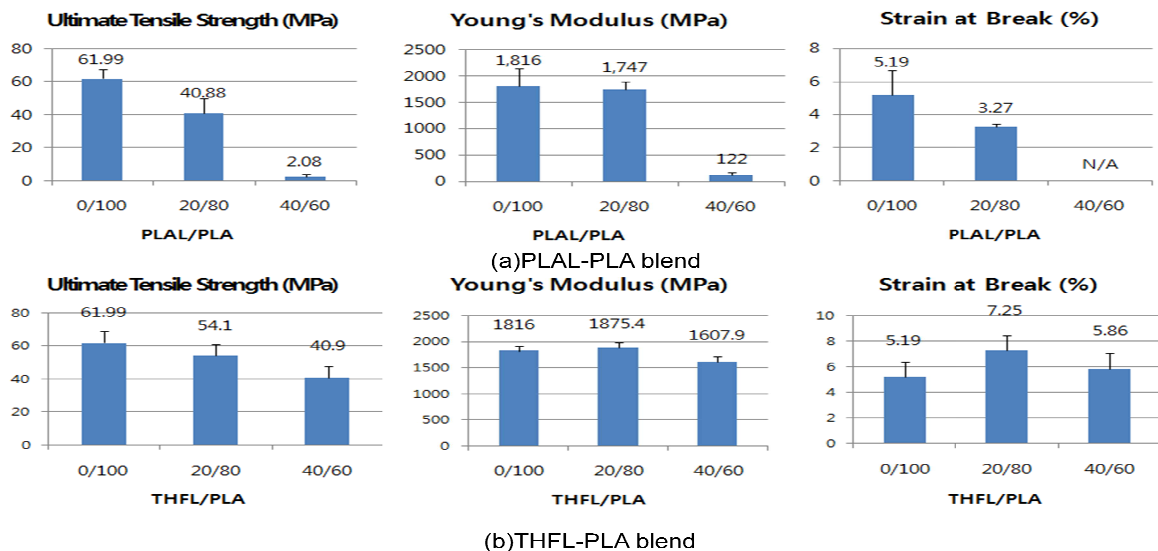


Figure 7. Mechanical properties of (a)PLAL-PLA blend and (b)THFL-PLA blend

All mechanical properties of PLAL-PLA is decreased by modification. Mechanical properties of 40:60 (PLAL/PLA) decreased remarkably while those of 20:80 decreased a little. THFL/PLA blends show the better mechanical properties that PLAL/PLA even though the good compatibility is expected in the case of PLAL/PLA.(Fig. 7.)

4. Conclusions

Modification of lignin can be confirmed by FT-IR and NMR analysis. Additionally, quantitative analysis of hydroxyl substitution is quantified by chemical reaction. However, chemical reaction analysis is impossible in this case because there is a hydroxyl group at the end of the alkyl chain used in this study. Therefore, FT-IR and NMR analysis are used as alternative methods of chemical reaction analysis.

The character of the alkyl chain used in the lignin modification in each blend was characterized by tensile properties measurement. These results show that the compatibility between the alkyl chain-matrix polymer is suitable for the intended usage. As same as tensile properties, thermal properties of the modified lignin/PLA blends are affected by the types of alkyl chain used in the lignin modification.

As a result, consideration of the alkyl chain-matrix polymer combination requires knowing which modified lignin was used as a filler or component of the composite materials. Furthermore, additional research about the properties of the alkyl chain is needed because the thermal and mechanical properties are very important factors in the proper use of polymeric materials.

Acknowledgement

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