

Chemical Modification of Kraft Lignin: Effect on Chemical and Thermal Properties

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Esterified kraft lignins (KL) were prepared by reaction with maleic anhydride (MA), succinic anhydride (SA), and phthalic anhydride (PA) in acetone solutions. The esterified lignins were characterized using ATR-FTIR, solid state CP-MAS ¹³C NMR spectroscopy, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). PA modification resulted in the highest weight gain percent (WGP) when compared to MA and SA modifications. Spectroscopic analysis revealed decreases in hydroxyl content and increases in carbonyl (C=O) and ester groups of the modified KL as a result of esterification. The hydrophobic properties of the modified lignin increased. The MA- and SA-modified KL showed an increased thermal stability compared to unmodified KL. PA-modified lignin presented distinct thermal decomposition stages, which showed rapid degradation at lower temperature. The results of this study indicate that it is possible to change the basic properties of kraft lignin by anhydride modification to facilitate the production of high performance composites.

Keywords: Kraft lignin; Organic anhydride; Esterification; Thermal stability; Composites

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INTRODUCTION

The incorporation of lignocellulosic materials as a reinforcing component in polymer composites has received increased attention, primarily as industry attempts to lessen the dependence on petroleum-based products. Inorganic fillers are being replaced by newer types of organic fillers (Bouza *et al.* 2008; Nath *et al.* 2010). Lignin, a complex organic phenolic polymer that is available in large quantities as industrial waste material from pulp and paper manufacturing, has become a promising alternative for this purpose. Neagu *et al.* (2006) investigated the stiffness contribution of various wood fibers to composite materials. They observed a correlation between lignin content and longitudinal Young's modulus, and an optimal lignin content range for maximum fiber stiffness was recorded for softwood kraft fibers. The work revealed that the stiffest fibers are expected within an intermediate range of kappa number 30 to 50. At lower and higher lignin content, the effective stiffness of the fibers drops considerably for the softwood kraft fibers. Behrooz *et al.* (2011) used kraft lignin (KL) as a compatibilizer in wood flour-polypropylene composites. Their results indicated that lignin improved physical (short term water absorption) and mechanical properties (flexural modulus, flexural strength, and impact strength). However, mechanical properties deteriorate with lignin proportion because of low compatibility/miscibility of polar lignin in a nonpolar polymer matrix (Alexy *et al.* 2000; Toriz *et al.* 2002; Pucciariello *et al.* 2004). In addition, dimensional

stability, as well as biological degradation of those products, has been attributed to the presence of hydroxyl groups in lignin.

These lignin issues open potential new areas to use modified lignin in a polymer matrix, which may increase compatibility/miscibility and introduce reactive sites of lignin. The available hydroxyl groups on the lignin molecule are reactive and plentiful in number. The modification of these reactive nuclei results in an effective alteration of the lignin solubility behavior. Increasing the length of the aliphatic chain can be expected to reduce the polarity of the KL and improve its solubility in nonpolar solvents. A number of reagents capable of forming stable covalent bonds have been studied as substitutes for these reactive hydroxyl groups. The major types of linkages formed by reaction with wood fiber are ether, acetal, and ester. Chemicals investigated to yield stable chemical bonds include alkyl or acid chlorides, anhydrides, carboxylic acids, epoxides, isocyanates, lactones, and nitriles. Pouteau *et al.* (2005) modified lignin by acid treatment and found that aliphatic content and polarity of treated lignin decreases. However, alkylated wood produced with alkyl chlorides contains acid residues, which adversely affect the mechanical properties. Among the many chemical modification reactions, acetylation and reactions with epoxides and isocyanates have been studied the most. Chemical modification of lignin with anhydrides renders the surface more hydrophobic. Acetylation of fiber greatly improves both mechanical strength and resistance to degradation due to ultraviolet radiation (Goldstein *et al.* 1961; Agarwal *et al.* 1985; Militz 1991). Some authors reported that esterified wood shows considerable reduction in swelling with improved anti-shrink efficiency, compared with unmodified wood (Rowell 1983, 1993; Wang *et al.* 2007).

Sailaja and Deepthi (2010) blended esterified lignin with low density polyethylene and found an increase in intermolecular interaction between the modified lignin and polymer matrix. Xiao *et al.* (2001) modified lignin using succinic anhydride to increase the thermal stability of lignin. Fernandez *et al.* (2006) modified lignin using phthalic anhydride and *p*-aminobenzoic acid and blended it with poly-(vinyl alcohol) to provide better thermal and photochemical properties. Modifying lignin with cyclic anhydride has been suggested as a way of introducing new material properties in which carboxylate groups (–COO–) can be linked through esterification or hydrogen bonding. Furthermore, the modification results in a pendant carboxylic moiety attached to lignin via covalent ester bond. Further studies could be beneficial using lignin in a pure form with known characteristics, because lignin composition varies from biomass to biomass and also depends on the chemical pulping process used during delignification (Henryk 1989). At present, a small number of significant techniques have been developed for commercial utilization of industrial byproduct lignin. Among the numerous chemicals investigated, acetic anhydride has proved to be one of the most effective reagents (Rowell and Tillman 1986; Militz 1991; Okino *et al.* 2004). As a linear chain anhydride, however, its reaction with hydroxyl groups yields acetic acid as a by-product, which creates an unpleasant odor and corrosion problems. In contrast, esterification with a cyclic anhydride causes a ring-opening, leaving a pendant covalently bonded carboxylic acid moiety attached to the lignin. Since the reactivity of the carboxylic groups is decreased after the ring-opening, cross-linking rarely occurs (Hill and Mallon 1998; Dawson *et al.* 1999). Although the proportion of diesters was found to increase above 120 °C, monoesters are still predominant in cyclic anhydride- modified wood (Matsuda 1987).

Maleic, succinic, and phthalic anhydride have been used primarily in previous studies on wood modification with cyclic anhydrides. Several European researchers

investigated the applicability of cyclic anhydrides without the presence of solvents. The general problem of solid state reactions is to accomplish an adequate contact between reagent and hydroxyl groups, along with a sufficient penetration into the wood itself. Therefore, organic solvents for full penetration into the wood cell wall were employed. In most studies, pyridine, DMF, or xylene has been used (Evans 1998; Hill and Mallon 1998; Suttie *et al.* 1998; Marchetti *et al.* 2000). These chemicals proved advantageous at laboratory scale but are unsuitable for larger-scale modifications for board manufacture because of their health and environmental effects as well as their price and difficult recovery. Dimethylsulfoxide (DMSO) has high swelling effect, which is advantageous for larger scale modification with cyclic anhydrides. However, the drawback is its high boiling point of 189 °C that makes recovery by evaporation/condensation systems difficult. Acetone, by contrast, has a boiling point of 57 °C, and it is a good solvent for MA, SA, and PA (Bodirlâu *et al.* 2008). It can also be washed away by water after the reactions. For these reasons, the present work addressed liquid state esterification with MA, SA, and PA in acetone with the objective to develop an economically feasible method.

The specific objective of the present work was to modify KL through chemical modification using organic anhydrides as the esterifying agents and to characterize the esterified lignin. ATR-FTIR and solid state CP-MAS ¹³C-NMR analysis were carried out to investigate the chemical changes after esterification. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were employed to study the thermal stability of the esterified KL and compare it with the unmodified control.

EXPERIMENTAL

Materials

The KL used in this research, which was derived from pine (*P. ponderosa*), was kindly supplied by Domtar, Plymouth mill, NC, United States. The general features of the sample were: dry matter 58.87%, ash content 0.45%, Klason lignin 85.47%, acid-soluble lignin 5.33%, total lignin 90.8%, and total carbohydrate 2.76%.

The organic anhydrides used as the esterifying agents in the study were maleic anhydride, succinic anhydride, and phthalic anhydride, sourced from Acros Organics (Fair Lawn, New Jersey).

Methods

Modification of KL

The KL sample was oven dried at 70 °C until reaching a constant weight (W_1). The sample was treated with maleic anhydride (MA), succinic anhydride (SA), and phthalic anhydride (PA), respectively. The esterification reactions were carried out as follows: the lignin was immersed in 10% solution of organic anhydride in acetone with the ratio of 1:20 (w/v). Afterwards, it was heated at reflux temperature (60 ± 2 °C) for 7 h in a reactor vessel provided with an agitator. At the end of the reaction, the reaction mixture was evaporated under vacuum to remove most of the acetone. The samples esterified with maleic anhydride were washed with distilled water; those with succinic anhydride were washed with hot water, while those with phthalic anhydride were washed with toluene to remove unreacted anhydrides and byproducts. They were then filtered through a pre-weighted crucible. Furthermore, the modified lignin was washed

successively with distilled water until neutral pH was reached. The products were then oven dried at 70 °C until reaching a constant weight (W_2).

The extent of reaction was calculated as weight percent gain (WPG) determined by the differences in oven dry weight of the sample before (W_1) and after (W_2) modification according to the following equation:

$$\text{WPG (\%)} = (W_2 - W_1) / W_1 \times 100 \quad (1)$$

To reduce errors and confirm the results, each experiment was performed in duplicate under the same conditions, and WPG represents the average value.

Characterization of the Modified Lignin

ATR- FTIR spectra

The surface chemistry of the esterified lignin was characterized by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy. ATR-FTIR was conducted on a Nicolet iZ10 module (Thermo Scientific, Verona, WI) using a Smart iTR Basic accessory. A single bounce, diamond crystal with 45° incident angle was used, and spectra were detected using a room temperature deuterated triglycine sulphate (DTGS) detector. Spectra were recorded in absorbance units, as an average of 64 scans in the range 4000 to 600 cm^{-1} at 4 cm^{-1} resolution.

CP/MAS ^{13}C -NMR spectra

The solid-state cross polarization-magic angle spinning (CP/MAS) ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DMX-400 spectrometer (Bruker Instruments Inc.) at a frequency of 125 MHz with a 5 mm MAS Broadband Observe (BBO) probe. Acquisition time was 0.034 s. The relaxation delay time was 2 s, the spectral width 30,303 Hz, and the proton 90 pulse time was 4.85 s. Each spectrum was obtained using an accumulation of 10000 scans. Chemical shifts were calculated relative to standard lignin molecules for spectrometer control.

Thermal analysis

Thermogravimetric analysis (TGA) of lignin and esterified lignin was carried out based on global mass loss with a PerkinElmer TGA 7 thermogravimetric analyzer (TA Instruments, New Castle, DE). The lignin was evenly and loosely distributed in an open sample pan, and the initial sample weight was about 5 to 7 mg. The temperature change was controlled from 100 °C to 700 °C with a heating rate of 10 °C/min. A high purity nitrogen stream with a rate of 20 mL/min was continuously passed into the furnace before thermal decomposition was carried out in order to prevent any unwanted oxidative decomposition.

Heat flux was determined using a DSC7 differential scanning calorimeter (Perkin Elmer, Waltham, MA, USA) linked to a thermal analysis controller TAC 7/DX. The scans were run at a heating rate of 10 °C/min under a nitrogen flow with the rate of 20 mL/min. The initial sample mass was 5 to 10 mg; aluminum pans were used. Before being tested, the samples were oven dried for 24 h at 70 °C to eliminate the presence of water. The lignin samples were heated to 200 °C and cooled at 40 °C/min to 40 °C. The glass transition temperature (T_g) was defined as mid-point of the temperature range at which the change in heat capacity occurs.

RESULTS AND DISCUSSION

Effects of Esterification on WPG

According to Farahani and Taghizadeh (2010), esterification with higher WPG significantly increased all the parameters. The WPG value is a common way to judge the amount of modification that has taken place (Abdul Khalil *et al.* 2001). The esterification of lignin hydroxyl bonds involves the nucleophilic attack on the acyl carbon centre of the anhydride molecule by an ion pair of the lignin hydroxyl group. Weight percent gain increased after modification with MA, SA, or PA. The preliminary results are illustrated in Table 1.

Table 1. Weight Percent Gain (WPG %) of MA-, SA-, and PA-modified KL

Anhydrides treatments	WPG (%)
Maleic anhydride	2.94 (± 0.33) [*]
Succinic anhydride	4.38 (± 0.26)
Phthalic anhydride	5.31 (± 0.37)

^{*}Numbers in parentheses represent the standard deviation of five replicates

Figure 1 (a, b, and c) displays the reaction schemes for maleic, succinic, and phthalic anhydride modification, respectively. Based on the results, KL modified with phthalic anhydride gave much higher WPG as compared to lignin treated with succinic and maleic anhydride. Comparison of WPG with the molar masses suggests that the anhydrides had similar OH-substitution rates (MA=98.02 g/mol, SA=100.04 g/mol, and PA=148.08 g/mol). The WPG revealed that reactivity of maleic anhydride was lower than that of succinic anhydride. In the case of MA- and SA-modification, the reason for WPG was due to adduction of a 4-carbon chain with carboxyl group to the lignin.

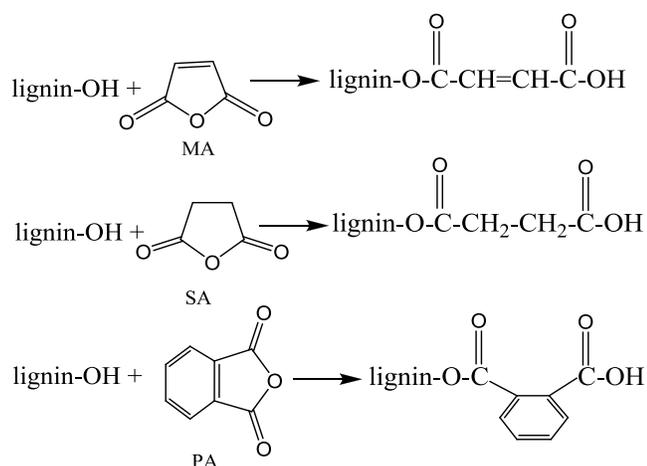


Fig. 1. Formula for lignin reacted with MA, SA, and PA for esterification

The WPG of succinylated lignin was slightly higher than maleated lignin due to the higher molecular weight of SA. Additionally, succinic anhydride is able to swell lignin more effectively, making reactive chemical sites more accessible and therefore, enhancing the reaction rate of modification, which results in higher WPG. The WPG of

the esterified KL was lower when compared to wood fiber. This could be due to the low swelling effect of acetone.

FTIR-ATR Spectra

Infrared spectra of the modified lignin samples were compared to spectra of unmodified lignin to establish the extent of esterification reactions (Figs. 2 and 3). The unmodified KL exhibited a strong broad peak at 3427 cm^{-1} (Fig. 3), which is attributed to the stretching of hydroxyl groups in phenolic and aliphatic structures. Esterification reactions with MA, SA, and PA resulted in decrease in the hydroxyl groups of lignin, along with the appearance of major absorption bands around 1713 cm^{-1} (C=O stretch). This indicated the formation of carboxylic acid through substituting hydrogen atoms of the hydroxyl groups with lignin and acetyl groups. Comparing the spectra of unmodified lignin to those of lignin modified with MA, SA, and PA shows the peaks at 1713 cm^{-1} were the dominant feature in the spectrum of esterified lignin samples (Fig. 2). This broad peak at $1680\text{--}1750\text{ cm}^{-1}$ is assigned to carbonyl stretching of ester and carboxyl groups in lignin, which indicated the existence of the carbonyl group (C=O) (Abdul Khalil *et al.* 2001). The increase of this peak gave evidence of anhydride modification.

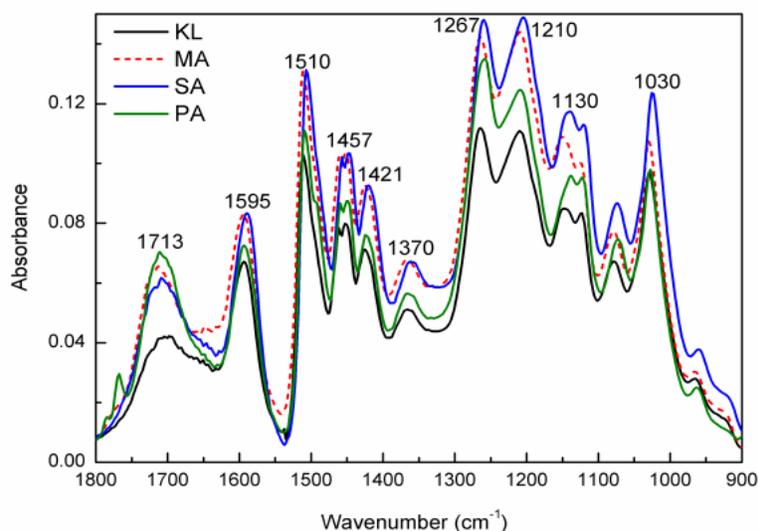


Fig. 2. FTIR-ATR spectra of the KL, and MA-, SA-, and PA-esterified lignin at the range of 1800 to 900 cm^{-1}

The FTIR spectra of lignin modified with SA and MA showed a more intense peak at 1713 cm^{-1} due to the esterification reaction. This observation was confirmed by an increase in the intensities of absorption peaks at 1267 cm^{-1} (C-O) and 1370 cm^{-1} (C-H). The peak at 1740 cm^{-1} , which is assigned to carbonyl bonds in esters, can be observed in PA-modified lignin.

The absorption at 2934 cm^{-1} , predominantly arising from CH stretching in aromatic methoxyl groups and in methyl and methylene groups of side chains, decreased after MA- and PA-modification, whereas no significant decrease was observed when treated with SA-modification. The peaks at 1595 , 1510 , and 1427 cm^{-1} are related to the aromatic skeletal vibrations, ring breathing with C-O stretching in lignin, and these also were enhanced by esterification. Succinylation and maleylation resulted in higher intensity of these peaks than those with PA. There was also a significant increase in

intensity of two ester vibration bands at 1130 and 1030 cm^{-1} after esterification. The strong band at 1030 cm^{-1} is assigned to C-O stretching in lignin. The band at 1130 cm^{-1} is characterized by the C-O antisymmetric stretching in the esters.

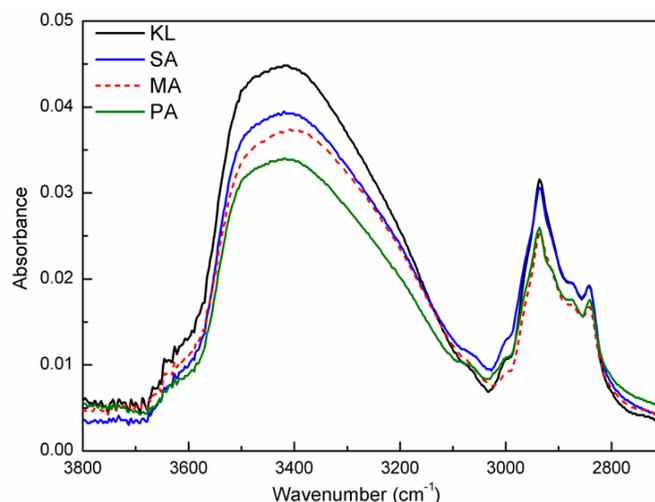


Fig. 3. FTIR-ATR spectra of KL, and MA-, SA-, and PA-esterified lignin at the range of 3800 to 2700 cm^{-1}

CP MAS ^{13}C NMR Spectra

CPMAS- ^{13}C NMR spectroscopy is the most effective of the few spectroscopic methods available for direct characterization of lignocellulosic materials and is capable of providing detailed information specific to solid samples (Love *et al.* 1998). Figure 4 shows the CPMAS- ^{13}C NMR spectra of unmodified KL, and MA-, SA-, and PA-modified lignin.

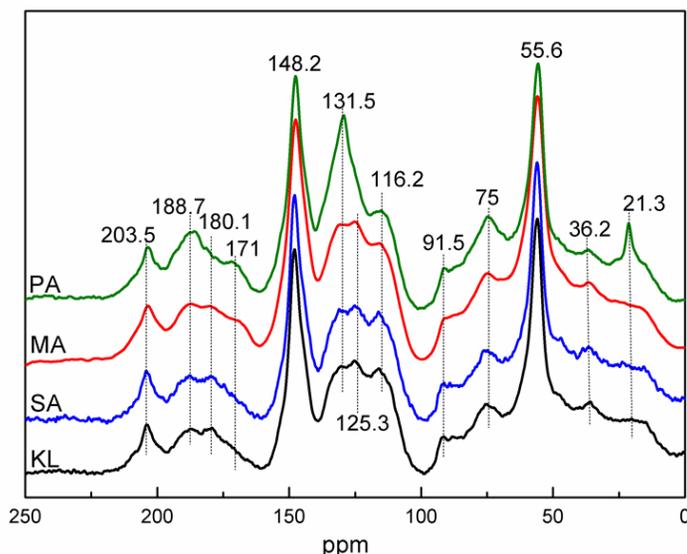


Fig. 4. CP-MAS ^{13}C spectra of the KL, and MA-, SA-, and PA-esterified KL

Aromatic carbon signals occur in the range of 100 to 155 ppm, while signals from aliphatic carbons occur between 20 and 90 ppm. The most prominent signal in the lignin ^{13}C spectra occurred at 55.6 ppm, attributed to methoxy carbons on guaiacyl and syringyl units (Fig. 4). Another major signal appeared at 148.2 ppm. These signals are due to the

C-3, C-4 on guaiacyl phenolic units and to C-3 and C-5 of syringyl units involved in β -O-4 structures (Beramendi-Orosco *et al.* 2004). The intensity of signals in the lignin region were strengthened after modification, which indicates a reaction of lignins with maleic anhydride, succinic anhydride, and phthalic anhydride.

The carbonyl group (C=O) at 171.0 ppm was increased with MA- and PA-modification compared to untreated KL. These peaks at 188.7 and 131.5 ppm increased significantly upon PA-modification. The increasing relative intensity of this signal from PA-modified KL was consistent with the WPG data in Table 1. The small peaks at about 180.1 ppm may be assigned to the -COOH carboxyl groups. These peaks decreased with MA and SA modification, and they almost disappeared after PA modification. Solid state ^{13}C CP-MAS NMR spectroscopy of PA-modified lignin showed a strong signal at 131.5 ppm, which resulted from the linkages between lignin and PA molecules. Signals corresponding to ester linkages at C_γ of lignin structure ($C_\gamma\text{-OR}$) were also identified at 75 ppm. An increase in the $C_\gamma\text{-OR}$ peak upon succinylation suggested that esterification occurred at the aliphatic hydroxyl groups of KL. The region from 170 to 160 ppm, representing esters and anhydrides, increased in intensity throughout esterification of lignin. This indicates that lignin structures undergo fairly rapid crosslinking reactions involving formation of esters and anhydrides. The esterification of lignin with anhydrides allows for the possibility of adduct being bonded to both aliphatic and phenolic hydroxyl groups via a monoester link or via a diester linkages. In the latter case a diester linkage may lead to crosslinking within the lignin. This is consistent with the increase in C=O groups associated with anhydrides and esters, as presented earlier in the FTIR data.

Thermal Analysis

The thermal properties of KL and its esterified derivatives were characterized using both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figs. 5 and 6). TGA curves reveal weight loss of lignin relative to temperature of thermal degradation, while the first derivative of the corresponding curve (DTG) shows rate of weight loss. The peaks of the DTG curve may be expressed as thermal decomposition temperatures, shown as T_1 , T_2 , and T_3 in Table 2. The temperatures at which the lignin samples attained various extents of degradation were evaluated. The onset degradation temperatures (T_0), and the temperatures at which 5, 10, 30, and 50% degradation occurred ($T_{5\%}$, $T_{10\%}$, $T_{30\%}$, $T_{50\%}$) are summarized in Table 2. It can be noted that PA-modified KL presented distinct decomposition stages from the unmodified KL, as well as MA- and SA-modified lignin. MA- and SA-modified KL showed an increase in thermal stability with the onset of degradation increasing from 156.6 to 159.4 and 170.4, respectively. This increase in onset degradation temperature for MA- and SA-modified KL was consistent with an increase in molecular weight. However, the T_0 decreased with phthalic modification with the initial onset of degradation occurring at the lower recorded temperature of 123 °C. The mass fell rapidly for PA-modified lignin as compared to untreated, MA- or SA-modified lignin. It is probably due to some toluene being left in the PA-esterified KL, which was not removed completely in the course of drying at 70 °C. The weight loss at much lower temperature may due to the evaporation of toluene.

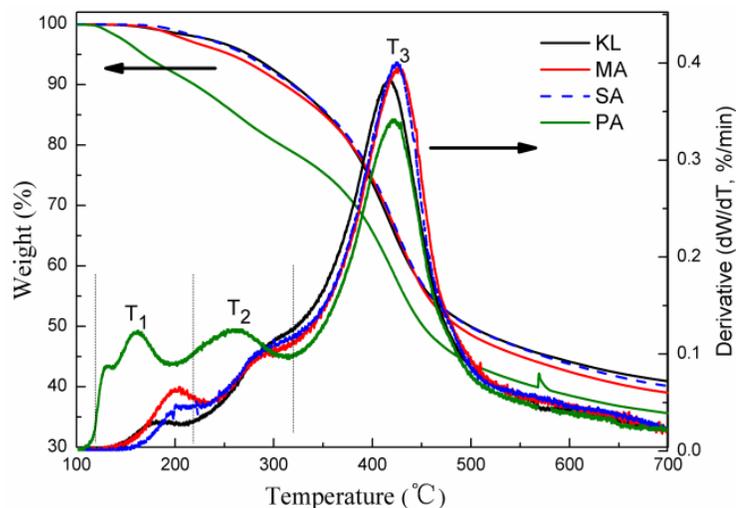


Fig. 5. TGA and DTG curves of the KL, and MA-, SA-, and PA-esterified KL

Table 2. Thermogravimetric Results of the KL, and MA-, SA-, and PA-esterified Lignin

	T_0	T_1	T_2	T_3	$T_{5\%}$	$T_{10\%}$	$T_{30\%}$	$T_{50\%}$
KL	156.6	180.0	290.2	417.5	278.5	322.0	409.7	497.8
MA	159.5	203.3	292.6	427.0	257.1	309.3	413.2	485.4
SA	170.4	220.9	298.7	425.7	271.4	320.1	414.1	495.6
PA	122.8	160.6	258.8	420.0	168.2	221.2	383.5	451.1

Comparison of the DTG thermograms of unmodified lignin and those with MA- and SA-modified products yielded similar observations, in contrast to PA-modified lignin. MA- and SA- modification of KL also raised the second and major decomposition temperatures T_2 and T_3 . PA-modification resulted in much lower T_2 , but a slightly higher T_3 . The decomposition at T_2 of the anhydride-modified lignin was previously described as the rupture of ester groups (Jakab *et al.* 1997). For KL, this ester group loss occurred with a maximum rate of decomposition observed at approximately 290 °C. At 5% or 10% weight loss the decomposition temperature was observed to occur at lower temperatures for MA-, SA-, and PA-modified KL than that unmodified lignin. It is interesting to note that decomposition of MA- or SA- modified KL samples shifted to a higher temperature at 30 and 50% degradation compared with unmodified lignin. It is known that the modification of lignin with anhydrides substitutes the hydrophilic hydroxyl groups with covalently bonded maleyl and succinyl groups, respectively, rendering the surface more hydrophobic. The increase in hydrophobic properties of the lignin was probably responsible for the observed improvement in thermal stability. The thermal stability of succinylated lignin was higher when compared with maleic modified lignin. This observation might be due to the possible formation of diester in addition to monoester cross-linked wood formations during succinylation. The possible reaction of cyclic acid anhydrides to form monoesters and diesters was reported by Matsuda (1987) and Hill and Mallon (1998). The anhydride-modified lignin may be useful as filler material to improve mechanical strength in plastics that are processed at temperatures up to 400 °C. This could expand possible areas of application, as process temperatures are well known to

limit the type of plastics that can be processed into wood polymer composites. The only exception is the modification of KL with phthalic anhydride, which resulted in lower thermostability in comparison with unmodified lignin.

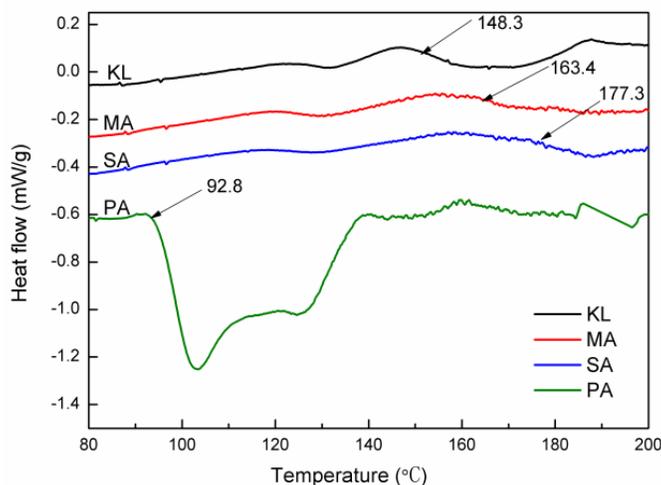


Fig. 6. DSC curves of the KL, and MA-, SA-, and PA-modified KL

DSC was used to determine the glass transition temperature (T_g) of the KL and its esterified derivatives. The glass transition of lignin is assumed to be in the middle portion of the enthalpy gradient as shown by the arrow mark on the DSC-curve (Fig. 6). It was observed that the glass transition temperature of KL was 148.3 °C, which increased to higher values of 163.4 °C and 177.3 °C for MA- and SA-esterification, respectively. The value decreased to 92.8 °C for PA-modification. This decrease in glass transition is essentially due to gains in the free volume of molecules as the ester substitution increases. Another explanation for the T_g depression may be the elimination of hydrogen bonds due to substitution of hydroxyl groups in lignin by ester substituent. This leads to increased mobility within lignin molecules and hence depression of the glass transition to lower temperatures. The data are in accordance with TGA results. Results for decomposition of MA- and SA-modified KL suggest improved thermal stability compared with unmodified lignin. Therefore the introduction of lignin in WPCs, especially those with higher thermal stability, will lead to higher thermal decomposition temperatures.

CONCLUSIONS

1. Among the esterification treatments, kraft lignin (KL) treated with phthalic anhydride gave much higher WPG compared to lignin treated with succinic and maleic anhydride. Esterification reactions resulted in a drastic decrease in the hydroxyl groups of lignin, along with an increase in carboxylic (C=O) and ester groups. Carbonyl bonds in esters can be observed in PA-modified lignin.
2. Lignin structures undergo fairly rapid crosslinking reactions involving formation of esters and anhydrides. This may make the lignin less hydrophilic and more compatible with thermoplastic matrices such as polyethylene or polypropylene.

3. Thermal stability increased at the major decomposition temperature for anhydrides-modified KL. PA-modified lignin presented distinct decomposition stages, which showed rapidly decreasing mass at lower temperatures. The glass transition temperature (T_g) increased for MA- and SA-modified lignin, but decreased for PA modification. This enhanced thermal behavior may suggest a wider temperature range of application for lignin reinforced wood plastic composites.

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