

# Spectroscopic Studies and Evaluation of Thermorheological Properties of Softwood and Hardwood Lignin

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**ABSTRACT:** Fourier transform infrared spectroscopy (FTIR) was used to determine characteristic absorption peaks of softwood kraft lignin and soda hardwood lignin. Remarkable spectral differences were noticed between the different lignins due to their various chemical structures. Proton nuclear magnetic resonance spectrometry ( $^1\text{H}$  NMR) was employed to analyze the structure of lignin. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) provided important data regarding the molecular weight distribution of lignin. Thermal stability of softwood lignin was found to

be remarkably higher than that of hardwood lignin. Softening temperature and glass transition temperature of lignin were measured by differential scanning calorimetry (DSC) which was useful in selecting an optimal temperature profile during extrusion process. Rheological studies provided valuable information about the viscosity of lignins. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 956–963, 2011

**Key words:** lignin; FTIR spectroscopy; molecular weight; thermal properties; rheological properties

## INTRODUCTION

Lignin is an aromatic heteropolymer that is mainly found in the secondary wall of wood cells.<sup>1</sup> As per Goring findings,<sup>2</sup> lignin is a random three-dimensional network polymer that is placed in the true middle lamella of wood and composed of phenylpropane monomers.<sup>3</sup>

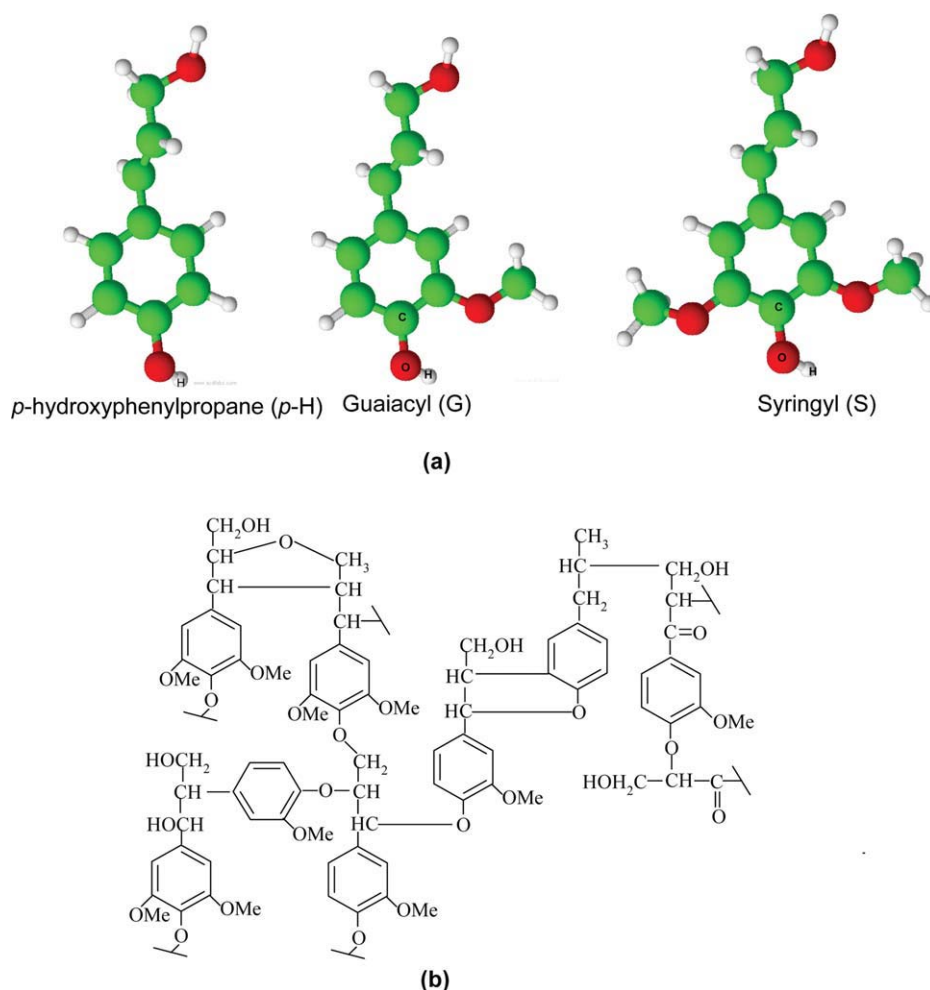
Lignin is the most abundant and important polymeric organic substance in the plant kingdom after cellulose.<sup>4</sup> Three different types of phenylpropane units are considered to generate the lignin by biosynthesis pathway. The three precursors of lignin are shown in Figure 1(a).

Guaiacyl precursor is made of coniferyl alcohol units; on the other hand, guaiacyl-syringyl precursors are from coniferyl and sinapyl alcohol. Chemically, softwood (conifers) lignins are mainly made of guaiacyl units whereas hardwood (angiosperms) lignins are consisted of guaiacyl-syringyl units.<sup>5</sup> Both lignins have dominantly glycerol-aryl ether ( $\beta\text{-O-4}$ ) linkages which works as crosslinks between short and linear chains of phenylpropane units.<sup>6</sup> The monomeric units of lignin are connected by carbon-carbon and ether linkages in different connecting

patterns which lead to the complexity of three dimensional structure of lignin.<sup>4,7</sup> The huge diversity of functional groups resulted in a complicated lignin macromolecule which is presented in Figure 1(b)<sup>8</sup> Lignins are the by-product of pulp and paper industries and it is readily available in nature. Most of the lignin is obtained from pulp and paper industry as byproduct. The application of lignin can be significantly varied depending on extraction technique and type of sources. Lignin can be used as dispersant, emulsifiers, ion-exchange resins, water treatment agent, pesticide surfactants, sequestering agents, binders, animal foods, grinding aids, electrolytic refining, and tanning agents, etc. Recently, lignin is being used as precursors of carbon fibers.<sup>9–12</sup> However, the structure of lignin is not completely understood yet. Over the last two decades, enormous studies have been conducted on lignin to figure out the industrial applications.<sup>8</sup> However, no detailed thermorheological properties of solid softwood and hardwood lignin were reported to date. Thermorheological properties of lignin play an important role to optimize processing condition and designing equipment during extrusion. Fourier transform infrared spectroscopy (FTIR) is found to be a very useful technique to characterize the lignin.<sup>13,14</sup>

In this study, fourier transform infrared spectroscopy (FTIR) was employed to characterize the functional groups in the softwood and hardwood lignin.  $^1\text{H}$  NMR was used to analyze the structure of

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**Figure 1** (a) Lignin precursors, and (b) Partial lignin structure proposed by Adler.<sup>5,7</sup>[Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

lignin. Molecular weight distribution of lignin was determined by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF). The thermal properties of lignin were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The rheological properties of lignin were determined using a twin bore capillary rheometer.

## EXPERIMENTAL

### Materials

Soda hardwood lignin (Eucalyptus) was obtained from GreenValue Company, Switzerland. The ash content of hardwood is  $\sim 0.4\%$  at  $800^\circ\text{C}$ . The lignin contains 61% of carbon, 6% of hydrogen and 33% of oxygen, respectively. Softwood kraft lignin (SKL) was obtained from Krugar, Wayagamack Inc. SKL contains 1.58% ash while heating the sample at  $525^\circ\text{C}$ .

### Methods

#### Fourier transform infrared spectroscopy

Lignin was mixed with oven dried KBr to avoid interferences due to the presence of moisture. Lignin KBr pellet was made by means of KBr pellet technique. Bruker FTIR model TENSOR 27 was used using 32 scans to investigate the IR bands and absorbance with respect to their functional groups of hardwood and softwood kraft lignin. Background spectra were taken in terms of every sample before getting sample spectra. Each spectrum was documented in the range of  $4000$  to  $400\text{ cm}^{-1}$  with a resolution of  $4\text{ cm}^{-1}$ .

#### Nuclear magnetic resonance

The chemical structure of SKL and HWL lignin was investigated through  $^1\text{H}$  NMR spectroscopy employing a Varian Unity Plus 500 MHz spectrometer at a frequency of 499.87 MHz for  $^1\text{H}$  (number of scans 16, delay 10 s, spectral width 7998.4 Hz and an

acquisition time of 2.70 s at ambient temperature). DMSO-d6 has been utilized as solvent.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry

Lignin samples were prepared in acetone/water (9 : 1v/v, 0.05 mg/mL). DHB (2, 5-dihydroxybenzoic acid) was used as matrix for this study to get optimum analytical results. Totally, 2  $\mu$ L of lignin and 2  $\mu$ L of matrix were mixed together in a plate. Totally, 1  $\mu$ L of sample was deposited on each well of the stainless steel multiple sample container and permitted to dry in air. The sample was completely dried in air before introducing in the mass spectrometer. Mass spectra were recorded after having 400 shots for softwood and hardwood lignin.

Thermogravimetric analysis

TGA was performed using TA instrument Q500 with a heating rate of 10°C/min. The samples were heated from 35 to 900°C to determine the complete thermal degradation of softwood and hardwood lignin. All tests were carried out in nitrogen atmosphere using a flowing rate of 60 mL/min.

Differential scanning calorimetry

The softening temperature of hardwood and softwood kraft lignin were investigated using a TA instrument Q1000 differential scanning calorimeter (DSC) attached with a cooling system under a nitrogen atmosphere. DSC instrument were run from 40 to 220°C with a heating rate of 10°C/min.

### Determination of flow property of lignin

The rheological properties of lignin were studied using a twin bore capillary rheometer (Rosand RH2000). A Flowmaster<sup>®</sup> software was used to analyze the rheological data of lignin. Bagleys's correction was used for the correction of entrance and exit pressure losses to provide the true wall shear stress. The sample was placed in the barrel of the extrusion system and pushed down into capillary with a plunger. The residence time of lignin in the barrel was 5 min and the melted lignin was extruded through the capillary at preselected plunger speed. The experiments were conducted at 225°C with different shear rate from 20 to 2000 s<sup>-1</sup>. The apparent shear rate ( $\dot{\gamma}_a$ ) and shear stress ( $\tau_w$ ) can be calculated from the eqs. (1) and (2).<sup>15,16</sup> The equations are as follows:

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \quad (1)$$

$$\tau_w = \frac{\Delta P \cdot R}{2L} \quad (2)$$

Where  $Q$  is the volume flow rate (cm<sup>3</sup>/s),  $R$  is the radius of the capillary,  $\Delta P$  is the pressure drop while conducting extrusion and  $L$  is the capillary length. The power law index is the exponent in the expression by the following equation.<sup>15,17</sup>

$$\tau_w = K \cdot \dot{\gamma}_a^n \quad (3)$$

Where  $k$  is the consistency index,  $n$  is the slope of the log  $\tau_w$  against log  $\dot{\gamma}_a$  plot. The flow behavior index is calculated as follows<sup>15,17</sup>:

$$n = \frac{d(\log \tau_w)}{d(\log \dot{\gamma}_a)} \quad (4)$$

Rabinowitsch correction is used to calculate the true wall shear rate by the given equation<sup>15</sup>:

$$\dot{\gamma}_w = \left( \frac{3n+1}{4n} \right) \dot{\gamma}_a = \left( \frac{3n+1}{4n} \right) \frac{4Q}{\pi R^3} \quad (5)$$

The true shear viscosity is termed as follows<sup>15</sup>:

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \quad (6)$$

## RESULTS AND DISCUSSION

### FTIR spectra of hardwood and softwood

A number of techniques have been developed to characterize the functional groups and structural properties of lignin. FTIR is one of the useful tools to determine the functional groups. FTIR can be applied for qualitative and quantitative measurements of intermolecular interactions in lignin.<sup>6</sup>

The peak positions of the IR bands and their relative absorbance in hardwood lignin and softwood kraft lignin are listed in Table I. The characteristic peaks of IR spectrum of hardwood lignin and softwood kraft lignin are shown in Figure 2.

In the finger print region (1800 and 900 cm<sup>-1</sup>), the spectral variation were observed in hardwood and softwood kraft lignin. The dominating spectra were detected at band positions 1511 and 1266 cm<sup>-1</sup> in the SKL lignin for aromatic skeletal vibration and guaiacyl ring breathing. As compared to SKL, the leading peak of hardwood lignin was noticed at bands 1510, 1213, and 1113 cm<sup>-1</sup>. The relative intensity of band at 1511 cm<sup>-1</sup> in softwood lignin was stronger than that of the bands 1614 (aromatic skeletal vibration breathing with C=O stretching) and 1458 (methyl and methylene deformation) cm<sup>-1</sup> of

**TABLE I**  
**Results of the IR Bands Obtained in Soda Hardwood (HWL) and Softwood (SKL) Kraft Lignin**

Serial No.	Hardwood	Softwood	Assignment
	Band position (cm <sup>-1</sup> )	Band position (cm <sup>-1</sup> )	
1	3433	3436	O—H stretching
2	2926	2922	C—H stretching
3	2849	2821	C—H stretching
4	1708	1701	C=O stretching (unconjugated)
5	1614	1598	Aromatic skeletal vibration + C=O stretching
6	1510	1511	Aromatic skeletal vibration
7	1458	1457	C—H deformation (methyl and methylene)
8	1427	1427	C—H in-plane deformation with aromatic ring stretching
9	1323	—	C—O of syringyl (S) ring
10	1260	1266	C—O of guaiacyl (G) ring
11	1213	1212	C—C + C—O stretch
12	1153	1146	Guaiacyl C—H and syringyl C—H
13	1113	—	Aromatic C—H in-plane deformation in the syringyl ring
14	—	1075	C—O deformation of secondary alcohols and aliphatic ethers
15	1032	1034	Aromatic C—H in-plane deformation (G>S)

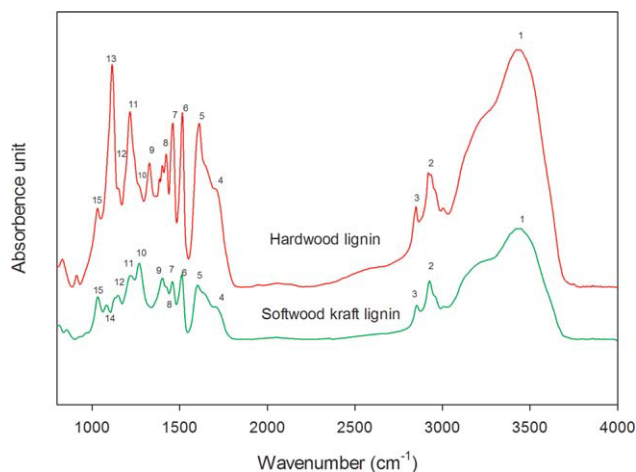
hardwood lignin. The absorption peak at 1113 cm<sup>-1</sup> (aromatic C—H in-plane deformation in the syringyl ring) was much greater than that of the 1032 cm<sup>-1</sup> band (C—H deformation in guaiacyl with C—O deformation in the primary alcohol) in hardwood lignin, whereas the intensity of the spectrum at 1034 cm<sup>-1</sup> was equal or higher than that of the 1113 cm<sup>-1</sup> in softwood lignin. A sharp intensity of band at 1266 cm<sup>-1</sup> was exhibited in softwood lignin, and there was no evidence of syringyl absorption at band 1323 cm<sup>-1</sup>, whereas a weak peak at 1260 cm<sup>-1</sup>, a strong peak at 1213 cm<sup>-1</sup> and a syringyl absorption peak at 1323 cm<sup>-1</sup> were appeared in the hardwood lignin. The greater intensity of spectrum at 1458 cm<sup>-1</sup> was proved the existence of a syringyl precursor in the hardwood lignin. The intensity of spectrum is observed at 1458 cm<sup>-1</sup> which was all most equivalent to the band intensity of hardwood lignin at 1511

cm<sup>-1</sup>. The absorption peak of guaiacyl type lignin was appeared at about 1266 cm<sup>-1</sup>, whereas syringyl absorption was visible at band 1323 cm<sup>-1</sup> in the hardwood lignin. Remarkable spectral differences were noticed in the hardwood lignin and softwood kraft lignin since the chemical structures of lignins were not identical. These results have well consistency with literature results was reported by Kubo et al. and Pandey et al..<sup>6,14</sup>

### NMR studies

The chemical structure of softwood and hardwood lignin was investigated by <sup>1</sup>H-NMR. the spectra of SKL lignin and HWL lignin are shown in Table II and Figure 3.

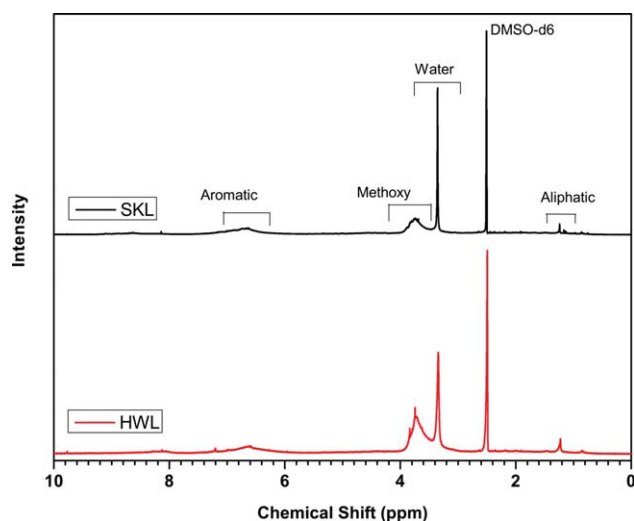
Two sharp signals at 2.5 and 3.3 ppm were viewed for solvent DMSO-d<sub>6</sub> and water, respectively. Table II showed signal assignments of both lignins. All signals between 6.0 and 8.0 ppm can be attributed to aromatic protons for S and G units which are shown in Table II. The aliphatic moiety of lignin was found to be in between 0.8 and 1.5 ppm. The aromatic protons in G and S units were observed at signal 7 and 6.6 ppm, respectively. The ratio of G to S is narrowly associated to methoxyl



**Figure 2** FTIR results of soda hardwood and softwood kraft lignin. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE II**  
**Signal Assignments of SKL and HWL Lignin by <sup>1</sup>H NMR Spectrometry**

Signal (ppm)	Assignment
6.0–8.0	Aromatic H in S and G units
7.0	Aromatic H in G
6.6	Aromatic H in S
3.1–4.2	H in methoxyl groups
2.3–1.9	Aliphatic hydroxyl H
0.8–1.5	Aliphatic H



**Figure 3**  $^1\text{H}$  NMR spectra of SKL lignin and HWL lignin. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

protons ( $-\text{OCH}_3$ ) which provided a sharp signal at 3.75 ppm. The ratio between G and S structures can be calculated by integrating various signal of  $^1\text{H}$ -NMR spectra while considering that the lignin is composed of only G and S units. Virtually there is also present *p*-H unit. As can be seen in Figure 3, the NMR methoxyl peak of HWL is higher than the peak of SKL due to presence of different G and S units.

### Molecular weight distribution studies by Maldi-TOF

MALDI-TOF mass spectroscopy is comparatively a novel spectroscopic technique which was applied to investigate the molar mass analysis of lignins. The mass to charge ratio of the ions formed by MALDI-TOF corresponded directly to the absolute molar mass of the analyte. The main drawback of MALDI-TOF is matrix signals which was appeared in the lower mass ranges.<sup>18</sup> Narrow molar mass distribution of lignin fractions was reported by Jacobs et al.<sup>19</sup> MALDI-TOF mass spectrum of softwood kraft lignin is shown in Figure 4. The mass spectrum showed a range of molecular weight from 80 to 617 Da (Dalton) providing sequences of signals (80, 92, 118, 145, 172, 190, 338, 379, 449, and 617) accordingly. No signals were detected after 617 Da. The center gravity of the distribution was appeared  $\sim 338$  Da. The distribution curve may be assigned possibly due to oligomeric lignin molecules. These oligomers were not identical. The interval of signals was observed from 12 to 68 Da.

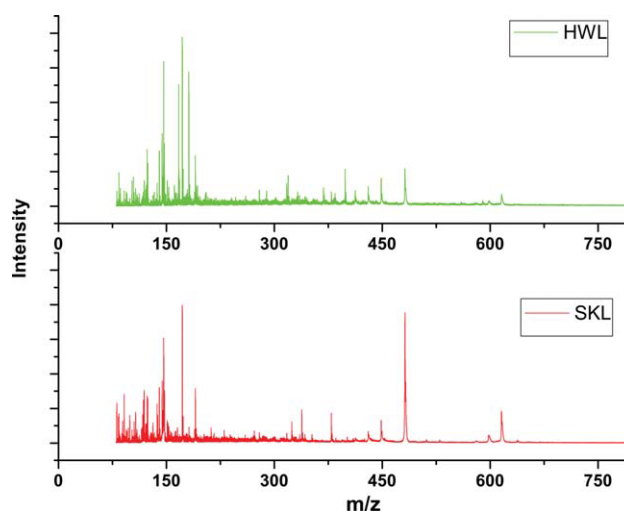
Apart from SKL lignin soda hardwood lignin was also investigated by MALDI-TOF spectrometer. Soda hardwood lignin exhibited almost similar molecular

weight distribution curves as compare to SKL lignin which is presented in Figure 4. Sequence of signals is 80, 124, 145, 166, 172, 181, 190, 317, 397, 429, 447, 481, 615 Da. Signals (397, 429, 447, and 481) were appeared possibly due to dimers. Only 615 Da was found probably due to trimers. Typical signal intervals were found to be in the range of 9–50 Da which was lower than that of SKL lignin. It should be noted that these results are in agreement with studies by Bocchini et al. and Metzget et al.<sup>7,20</sup>

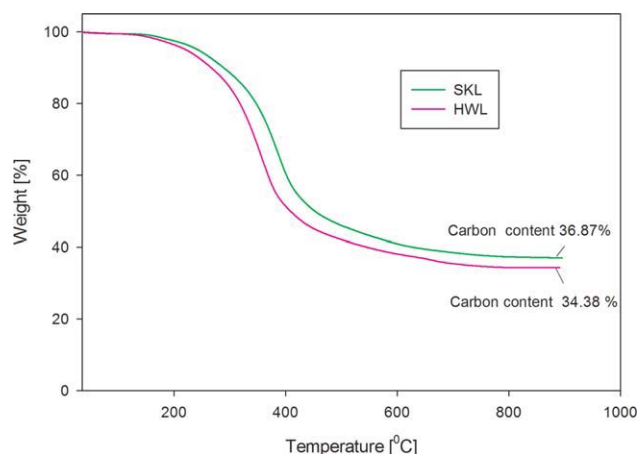
### Behavior of lignin during thermal treatment

When lignin was exposed at elevated temperature, significant physical and chemical changes can occur in lignin. The alteration in mass was obtained through dehydration, decomposition, and oxidation of specimen with respective to temperature and time.<sup>21</sup>

The thermal degradation of softwood kraft lignin and soda hardwood lignin is shown in Figure 5. Both lignins demonstrated low volatile contents and the weight loss of material (6–8%) occurred at 250°C. Hardwood lignin appeared to have the ash content of 0.4% at 800°C whereas SKL lignin exhibited the ash content of 1.58% at 525°C as per supplied material safety data sheet. The mass loss of lignin took place slowly under the temperature range of 150 to 900°C. The magnitude of mass loss was not evident in the temperature range of 35–150°C due to volatile contents. Dehydration reaction took place at 200°C which was principally accountable for lignin degradation. Cleavage of  $\alpha$  and  $\beta$  aryl-alkyl-ether linkages occurred between 150°C and 300°C. Separation of aliphatic side chains from aromatic ring was observed at  $\sim 300^\circ\text{C}$ . At last, the carbon-carbon



**Figure 4** MALDI-TOF mass spectra of soda hardwood lignin and softwood kraft lignin. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5** TGA results for softwood kraft lignin and soda hardwood lignin. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

linkages of lignin structural units were cleaved at 370–400°C. The decomposition reaction of both lignin was an exothermic reaction demonstrating between 225°C and 450°C. These results are in well agreement with the data reported by Van et al.<sup>22</sup>

The TG curve showed first weight loss step between 35 and 350°C and second mass loss step between 350 and 626°C for SKL lignin. A mass loss of 20% was determined between 35 and 350°C. The weight loss of SKL lignin was found to be ~ 60% during the second decomposition step. Similarly, hardwood lignin lost weight in two steps providing a mass loss of about 20 and 63% at 320 and 626°C, respectively. The softwood lignin lost weight slower than that of hardwood lignin since hardwood lignin contains more oxygen as compared to SKL lignin. The yield of carbon from softwood lignin was found to be ~ 36.87% at 900°C whereas hardwood lignin exhibited a carbon yield of 34.38% at 900°C.

### DSC observations

The thermal behavior of the material was studied using DSC technique. The endothermic and exothermic events, glass transition and heat capacity changes can be obtained by DSC studies.<sup>21</sup> The endothermic or exothermic event depends on the amount of heat flowing rate through the sample.

Glass transition temperature of lignins is always influenced by moisture content. The lignin sample was dried in an oven at 70°C for 24 h. The glass transition temperature of various underivatized lignin was ranged from 90 to 180°C. The higher value of  $T_g$  corresponded to softwood kraft lignin and lower ones to organosol lignin.<sup>8</sup>

The transition temperature of softwood lignin was greater than that of the hardwood lignin. DSC results of soda hardwood lignin and softwood kraft

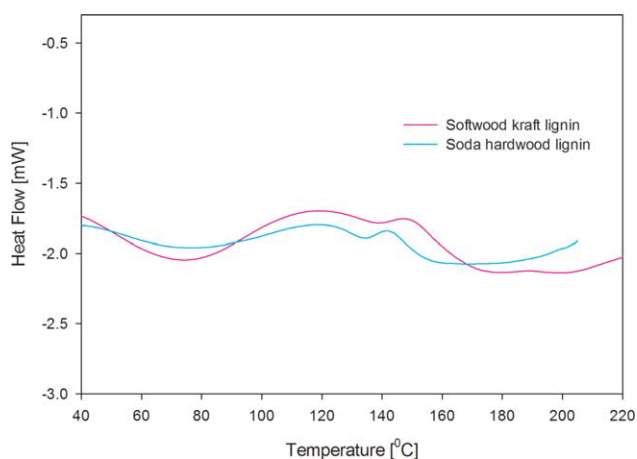
lignin are shown in Figure 6. The glass transition temperature ( $T_g$ ) of HWL was 93°C, whereas  $T_g$  of softwood lignin was appeared at 100°C. Endothermic reactions occurred in both lignins. It is clearly observed that  $T_g$  of SKL was much higher than that of HWL lignin. The exothermic event was observed at 141°C for HWL lignin followed by the softening temperature at 188°C. Similarly, a sharp exothermic peak was viewed at 148°C for SKL lignin. The softening temperature of SKL lignin was ~ 200°C.

### Flow properties of softwood and hardwood lignin

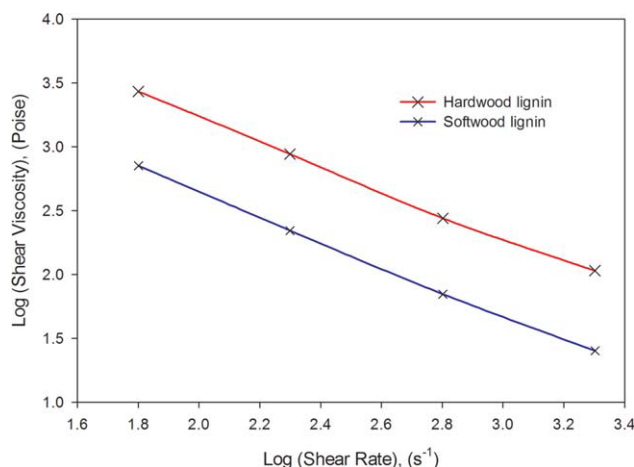
The rheology of polymer is important to optimize the processing conditions and designing the different parts of instrument including extruder, die and melt spinning equipment.<sup>15</sup> The flow properties of lignin offer an important data regarding viscosity that is helpful in determining an optimum processing condition during extrusion of lignin.

In this study, the flow behavior of softwood lignin and hardwood lignin were investigated with different shear rates and a temperature of 225°C. Shear flow properties of lignin can be characterized by flow curves where shear viscosity is a function of shear rate. Generally speaking, the polymer solutions are non-Newtonian character. The rheological properties of the polymer depend on the shear rate and temperature. The non-Newtonian character of polymer has a great influence in developing lignin fiber or lignin based composite materials.

As shown in Figure 7, the viscosity of softwood and hardwood lignin was reduced with increasing shear rate demonstrating shear thinning behavior, and the variation of viscosity between softwood and hardwood lignin were significantly decreased. In the low shear rate domain, softwood and hardwood lignin also demonstrated a considerable difference



**Figure 6** DSC curve for softwood kraft lignin and soda hardwood lignin. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 7** Relation between shear viscosity and shear rate of lignins at 225°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

between the shear viscosities of lignins. So it is obvious that both lignins have shear dependence viscosity. The viscosity of softwood and hardwood lignin was found to be considerably different in the low and high shear rate region due to their different chemical structures and molecular weights.

The melt flow behavior index ( $n$ ) is a vital factor while studying non-Newtonian character of polymeric fluids. The flow of lignins was pseudoplastic.

It is obvious from Table III, increasing shear rate resulted in increased the melt flow behavior index ( $n$ ) of softwood and hardwood lignin when extrusion conditions are constant. A smaller  $n$  value means a stronger non-Newtonian character which corresponded to greater shear thinning behavior. It is quite clear that the shear rate significantly affects on the shear viscosity with a non-Newtonian character. Both lignin presented lower flow behavior index ( $n$ ) indicating lower flow properties and non-Newtonian character. Since  $n$  value is lower for both lignin, therefore it is recommended to utilize plasticizing agent or other polymer additives to maintain the flow behavior of lignin during extrusion. It can be summarized that the viscosity of softwood and hardwood lignin can also be controlled by adjusting shear rate during extrusion or melt spinning with a suitable temperature.

**TABLE III**  
Flow Behavior Index ( $n$ ) of Softwood and Hardwood Lignin Melt

	Softwood lignin	Hardwood lignin	Shear rate (s <sup>-1</sup> )
$n$	0.02	0.03	199.17
	0.06	0.09	633.78
	0.09	0.15	2006

## CONCLUSIONS

Characteristic absorption peaks were determined for softwood kraft lignin and soda hardwood lignin by FTIR. The dominating spectra were observed at band positions of 1511 and 1266 cm<sup>-1</sup> in the SKL lignin due to aromatic skeletal vibration and guaiacyl ring breathing with carbonyl stretching. As compared to SKL, the leading peak of hardwood lignin was noticed at bands 1510, 1213, and 1113 cm<sup>-1</sup>. Remarkable spectral differences were observed in soda hardwood lignin and softwood kraft lignin since the chemical structures of lignins are not identical. The chemical structure of softwood and hardwood lignin was investigated by <sup>1</sup>H NMR. Spectra of lignins were found to be dissimilar because of G and S units. The results presented in this study showed that MALDI-TOF is a good technique which provided valuable information on the oligomeric distribution of lignins. However, the spectrum of MALDI-TOF did not provide the higher molecular weight distribution of lignins. Softwood kraft lignin and soda hardwood lignin were analyzed by TGA. The decomposition process was found to be two steps. The yield of carbon in softwood kraft lignin was estimated to be about 36.87% at 900°C whereas soda hardwood lignin provided a carbon yield of about 34.38% at identical temperature. DSC observations provided the softening temperature of both lignins which will be useful to choose an optimal temperature profile to process lignin in an extruder. Also, DSC results detected the glass transition temperature and exothermic events for all lignins. Rheological studies showed that the viscosity of softwood kraft lignin and soda hardwood lignin reduced with increasing shear rate demonstrating shear thinning behavior. Both lignin presented lower flow behavior index ( $n$ ) indicating poor flow properties and non-Newtonian character. The rheological properties of SKL and HWL lignin provided an important data regarding viscosity that is helpful in determining an optimum processing condition during the development of lignin fibers or lignin based composite material.

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