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Optimum Conditions for Selective Separation of Kraft Lignin

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ABSTRACT

Lignin has been investigated over the last few decades as a promising natural alternative to phenolic resin (phenol-formaldehyde), due to their structural similarity. In the present work, lignin was precipitated from the Kraft black liquor of *Eucalyptus camaldulensis Dehn*. at pH 2, 4 and 6, respectively in order to determine the optimal separation conditions. A comparison study was performed among the lignin samples obtained, based on yield, average molecular weight, chemical structure and thermal stability. The results showed that the best conditions occurred with lignin precipitation at pH 4. For low molecular weight (MW) lignin, each selective extraction was carried out using dichloromethane, acetone and methanol to study the effects of the lignin to solvent ratio, and extraction time on the lignin yield. Physico-chemical characterization of the low MW lignin was also carried out to evaluate the most suitable lignin for adhesive purposes. The results showed a ratio of 1:5 (lignin:solvent) and an extraction time of 1 h were sufficient for extraction. Dichloromethane-soluble lignin with a molecular weight of approximately 940 g mol^{-1} would be best for the adhesive formulation in future work.

Keywords: kraft lignin, optimum condition, selective extraction, physico-chemical properties

INTRODUCTION

Phenolic-based resins, including urea formaldehyde (UF) and phenol formaldehyde (PF), are the most commonly used binders in the wood composite industry. However, one of the disadvantages of PF is its formaldehyde emission, which is important from the point of environmental pollution. Thus, the adhesive industry has been trying to find alternative binders for wood composite products. In recent years, bio-based materials have attracted considerable attention, as concern has grown for environmental protection. A number of studies have been carried out to reduce or replace the phenol and formaldehyde contents in adhesive formulations or to develop adhesives from natural materials, such as soy protein adhesives (Kumar *et al*., 2002; Liu and Li, 2002), the upgrading of vegetable tannin adhesives without aldehydes or hardeners (Li *et al*., 2004; Lei *et al*., 2008), a chitosan-phenolic system (Peshkova and Li, 2003), a starch-based wood adhesive (Imam *et al*., 2001) and a bark-based adhesive (Alma and Kelley, 2000). Lignin is also one of the natural components used to produce such modified binders, because of its ready availability and the similarity between the structure of lignin and that of PF. In addition,

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lignin-based resin is not only environmentally friendly, but also less expensive. The literature on the use of lignin to prepare wood adhesives is very extensive (V·zquez *et al*., 1997; Khan *et al*., 2004; El Mansouri *et al*., 2007; Tejado *et al*., 2007). It has been found that the characteristics and properties of lignin are very dependent on the original source and the extraction method, leading to different final adhesive behavior. Therefore, prior to the adhesive synthesis, such knowledge is considered of importance.

Lignin is a complex phenolic polymer occurring in higher plant tissues and is the second most abundant polymer after cellulose. It is a waste product of the pulp and paper industry. Among a number of different pulping processes, Kraft pulping is the most commonly used chemical pulping process, accounting for more than 80% of the chemical pulp produced in the world (Sjöström, 1993). From previous work, Kraft lignin is known to be more reactive in formation with formaldehyde than other lignins, due to its higher content of phenolic hydroxyl groups and low methoxy groups (Nada *et al*., 1998). However, one of the disadvantages of lignin-based resins compared to PF resin is that they generally tend to have weaker adhesion properties and to have a high degree of variability in adhesion performance. Apart from the structural aspect of lignin, its molecular weight also affects formation reaction. In general, a small molecule is known to be more reactive than a larger one.

The main purpose of the project, a part of which is presented here, was to assess the possibility of developing a lignin-based adhesive that could perform well with regard to the requirements of the wood composite industry. Firstly, the study attempted to optimize the separation conditions for the Kraft lignin with its low MW. Secondly, to gain a better understanding of all lignin samples obtained prior to the adhesive formulation, a complete characterization of the samples was carried out using: 1) Fourier transform infrared spectroscopy (FT-IR), to analyze their chemical structure; 2) gel permeation chromatography (GPC), to determine molecular weights and their distribution; 3) differential scanning calorimetry (DSC), to measure the glass transition temperature; and 4) thermogravimetric analysis (TGA), to quantify the thermal degradation.

MATERIALS AND METHODS

Materials

Kraft black liquor of *Eucalyptus camaldulensis Dehn*. used in this study was obtained from a commercial wood pulp manufacturer in Thailand. The Kraft black liquor had a total sulfur content as sulfate (SO_4^{2-}) of 8-9%.

Optimum pH for lignin separation from black liquor

The Kraft lignin was precipitated from the black liquor by acidifying to various pH levels (2, 4 and 6) using concentrated sulfuric acid (Figure 1). The precipitated lignin was then filtered and washed with water until a neutral pH was obtained. Then, the Kraft lignin obtained was dried in an oven at 55°C for 24 h prior to further analyses. All experiments were carried out in triplicate.

Selective extraction of low MW lignin

The process used to isolate the soluble lignin is shown in Figure 1. Briefly, about 2.5 g of Kraft lignin precipitated from the black liquor at pH 4 was mixed with dichloromethane (25 mL) and stirred vigorously for 1 h at room temperature. The undissolved solid was filtered and discarded. The dichloromethane fraction was evaporated to dryness in order to obtain the dichloromethane-soluble lignin (Extract 1).

The preparation systems and conditions described above were also used in the extraction

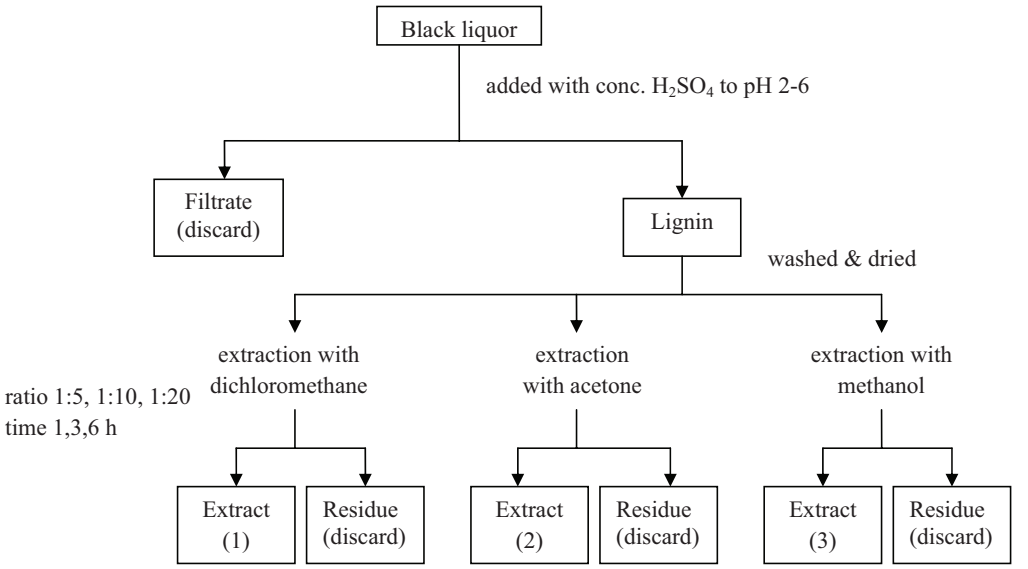

Figure 1 Schematic diagram for precipitation of lignin from Kraft black liquor of *Eucalyptus camaldulensis Dehn.* and selective extraction of low MW lignin with dichloromethane, acetone and methanol.

of lignin with acetone and methanol to obtain the acetone- and methanol-soluble lignin (Extract 2 and Extract 3, respectively). The extraction time (1-6 h) and the ratio between the lignin and organic solvent (1:5, 1:10, and 1:20 w/v) of each system were varied in order to study the influences of these parameters on properties of the lignin obtained. All experiments were carried out in triplicate.

Analytical methods

Dry matter content

The dry matter content was gravimetrically determined after drying samples at 105°C for 16 h to constant weight.

Ash content

The ash content was gravimetrically determined after incineration at 550°C for 6 h.

Average molecular weight and molecular weight distribution

The lignin was completely dissolved in THF (tetrahydrofuran, 5 mg/mL) at room temperature overnight, with gentle stirring. Then, the lignin solution was filtered through a membrane (0.45 μm, pore size), before being injected into the GPC system. The system consisted of three Styragel columns (7.8 mm ID × 300 mm, Waters, the Netherlands). Size exclusion was performed at room temperature with THF as the mobile phase (flow rate 1.0 mL/min) and an RI (refractive index) detector. Calibration was performed with polystyrene standards with MW values ranging from 99 to 188,000.

FT-IR spectroscopy

The FT-IR spectra of lignin samples were recorded from KBr (potassium bromide) discs containing 1% finely ground samples on an FT-IR/FT-Raman spectrophotometer (Perkin Elmer System 2000) in the wavenumber range of 4000-400 cm^{-1}.

Thermal properties

TGA was performed with about 3 mg of lignin using a Mettler Toledo TGA/SDTA 851^e with a heating rate of 10°C/min under helium atmosphere. The temperature ranged from ambient to 800°C.

DSC analysis was conducted using a

Mettler Toledo DSC 822^e. Approximately 6 mg of lignin sample was placed in an aluminum pan and sealed with an aluminum lid. The reference was an empty aluminum pan. The samples were heated from -5 to 350°C at a rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Optimum pH for lignin separation

The Kraft black liquor of *Eucalyptus camaldulensis Dehn.* used in this study had an initial pH of approximately 12. The Kraft lignin was precipitated after adding sulfuric acid and the percentage yield of lignin following precipitation at various pH levels (2-6) are shown in Table 1. As would be expected, the yield of lignin depended on the precipitation pH, which was consistent with other reported results (Sun *et al.*, 1999; Garcia *et al.*, 2009). It has been found also that decreasing the pH results in an increase in recovered lignin, indicating that a lower pH tended to favor lignin recovery from the black liquor. For instance, there was an optimal precipitation pH of 2 for the recovery of lignin from the black liquor resulting from pulping the fiber in oil palm without fruit bunches, using 20% KOH and 0.1% anthraquinone (Sun *et al.*, 1999). Moreover, it has been reported that lignin from soda pulping black liquor (7.5% NaOH) of *Miscanthus sinensis* precipitated at pH 2.57 exhibited similar characteristics to commercial alkaline lignin, even though the highest yield was found at pH 4.55 (Garcia *et al.*, 2009).

On the other hand, from the results shown in Table 1, the optimum pH for lignin separation from the Kraft black liquor of *Eucalyptus camaldulensis Dehn.* seemed to be pH 4.0, since, at this pH, the highest yield of lignin (about 23%) was obtained with identical characteristics (ash content, MW, FT-IR spectra, and thermal properties) to those at pH 2.0. In contrast, the precipitation at pH 6.0 gave the lowest lignin yield with a greater amount of impurities indicated by the much higher ash content. Hence, the Kraft lignin precipitated at pH 4.0 was selected for the selective extraction with various solvents in the next step.

Optimum condition for selective extraction of low MW lignin

Since lower MW lignin samples are more soluble in organic solvents than higher MW samples and are suitable for the synthesis of a lignin-based adhesive, selective extractions were performed on the lignin precipitated at pH 4.0 using various types of organic solvents (dichloromethane, acetone and methanol). The influence of extraction time (1, 3, and 6 h) and the ratio of lignin to solvent (1:5, 1:10, and 1:20) on the percentage yield and properties were studied. As shown in Table 2, it seemed to be possible to produce low MW lignin extracts from the solvents within 1 h. The % yields of the low MW lignin soluble in dichloromethane, acetone and methanol were approximately 26, 85 and 87%, respectively. It was notable that there was not much difference in the amount of low MW lignin extracted by acetone and methanol. This probably resulted from the similar polarity of acetone and methanol, in contrast to dichloromethane. The effects of the lignin to solvent ratio on % yield, are shown in

Table 1 Percent yield and ash content of the Kraft lignin obtained using various pH levels.

pH	Yield of lignin* (%)	Ash content (%)
2.0	20.52 ± 0.60	0.04 ± 0.02
4.0	22.82 ± 0.64	0.04 ± 0.01
6.0	12.51 ± 0.82	1.67 ± 0.10

* Based on total dry solid of black liquor.

Table 3. Again, there was not much difference in the % yield of low MW lignin at various ratios (1:5, 1:10 and 1:20). The % yields of low MW lignin were also similar to those obtained from the study on the effect of the extraction time.

Overall, an optimum condition for extraction of the lower MW lignin with the studied solvents was 1 h extraction time with a ratio of lignin to solvent of 1:5. To clarify whether, from a similar content obtained, the soluble lignin samples extracted with acetone or methanol were the same substance, further investigation, studying their MW and thermal properties, was performed.

Average molecular weight and distribution

Table 4 shows average molecular weights (M_w, weight-average molecular weight and M_n, number-average molecular weight) and the molecular weight distribution (indicated as polydispersity = M_w/M_n) of lignin obtained from various conditions. The lignin samples precipitated at pH levels from 2 to 6 exhibited no significant difference in their average molecular weight between 1,418 and 1,535 g mol^{-1}. These values are quite low, resulting in their complete dissolution in THF without acetylation derivatization before GPC analysis. The low MW may be the result of significant degradation of β-aryl ether during the cooking process. In addition, the results demonstrated that all lignin samples had relatively narrow molecular weight distribution, as indicated by polydispersity values less than 2,

Table 2 Percent yield of soluble lignin in various solvents at various extraction times.

Time (h)	Yield of lignin * (%)		
	Dichloromethane	Acetone	Methanol
1	25.47 ± 0.26	85.31 ± 0.96	86.86 ± 0.58
3	25.63 ± 0.10	83.35 ± 0.23	87.75 ± 0.16
6	26.62 ± 0.04	86.12 ± 0.95	87.67 ± 0.26

* corresponding to the lignin samples in Figure 1, with a constant ratio of lignin and solvent 1:10 (w/v).

Table 3 Percent yield of soluble lignin in various solvents at various lignin/solvent ratios.

Lignin/solvent ratio (w/v)	Yield of lignin % (%)		
	Dichloromethane	Acetone	Methanol
1 : 5	24.01 ± 0.31	87.83 ± 0.81	86.74 ± 1.10
1 : 10	25.47 ± 0.26	85.31 ± 0.96	86.86 ± 0.58
1 : 20	26.91 ± 0.08	87.37 ± 0.41	85.06 ± 0.85

* corresponding to the lignin samples in Figure 1, with a constant extraction time 1 h.

Table 4 Molecular weight of lignin obtained from various conditions.

Lignin*	Average MW (g mol^{-1})		Polydispersity
	M_w	M_n	
Precipitated at pH 2	1455	1098	1.33
Precipitated at pH 4	1418	1071	1.32
Precipitated at pH 6	1535	1104	1.39
Extract (1) : dichloromethane	942	791	1.19
Extract (2) : acetone	1474	1085	1.36
Extract (3) : methanol	1363	1052	1.29

* corresponding to the lignin samples in Figure 1.

which confirmed that all samples possessed a high fraction of low molecular weight. The polydispersity increased slightly with increasing molecular weight. This was in accordance with the results obtained by Yuan *et al.* (2009) in a study of *Eucalyptus pellita* lignin fractionated from Kraft-anthraquinone black liquor (Yuan *et al.*, 2009). In contrast, higher MW and polydispersity of lignin from soda black liquor of Alfa grass (Hattalli *et al.*, 2002) and of *Miscanthus sinensis* (Garcia *et al.*, 2009) were observed. Higher polydispersity was observed when the soda black liquor of Alfa grass was treated with HCl at pH 2 rather than when treated at pH 4. In addition, there was a higher total phenolic content in lignin precipitated at pH 2 (Hattalli *et al.*, 2002). Overall, it can be concluded that the cooking condition might be one of crucial parameters leading to different degradation of lignin, different MW values and polydispersity.

For the selective extraction of low MW lignin with various solvents (dichloromethane, acetone and methanol), it was found that among all samples, there were no significant differences in MW, except for the sample extracted from dichloromethane. The starting lignin precipitated from black liquor at pH 4 and lignin extracted with acetone and methanol possessed similar MW values ranging from 1,363 to 1,474 g mol^{-1}, whereas lignin extracted from dichloromethane possessed lower M_w (942 g mol^{-1}). Lignin with a high fraction of lower MW molecules is more suitable for condensates with phenol formaldehyde, because it is more reactive than with high MW molecules (Pizzi, 1994). Thereby, it seemed to be possible to use the dichlormethane-soluble lignin in the formulation of a lignin-based resin/adhesive.

FT-IR

It is well known that the delignification method used for the isolation of lignin plays an important role in the final structure of lignin. It was considered important to investigate whether structural changes in the lignin would result from various conditions. FT-IR has been shown to be a useful tool in monitoring structural changes in polymers. The FT-IR spectrum and corresponding assignment of lignin are shown in Figure 3 and Table 5, respectively. The results showed that the FT-IR spectra of all lignin samples were very similar, indicating that there was a similar core structure of lignin. The band at 3390 cm^{-1} seemed to be a characteristic of the phenolic-OH groups

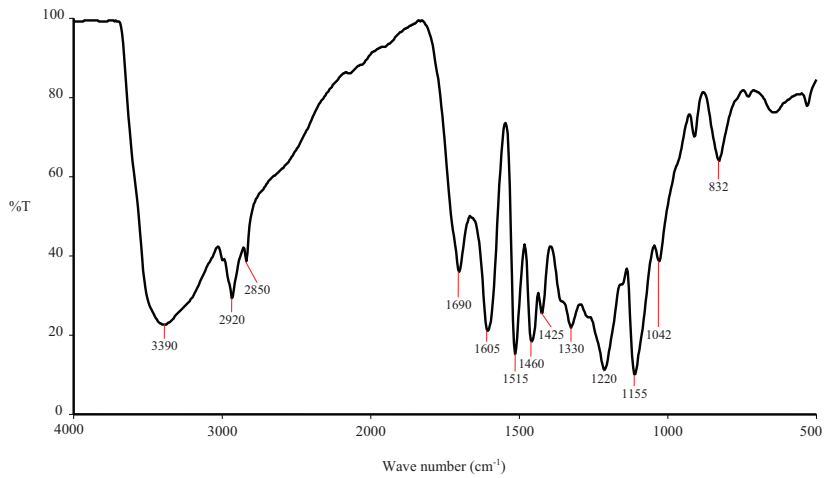

Figure 2 FT-IR spectrum of lignin. Similar spectra were obtained for lignin precipitated at pH 2-6, including the low MW lignin extracted with dichloromethane, acetone and methanol.

of lignin, while the band at 2920 cm^{-1} was attributed to C-H stretching of the $-CH_3$ or $-CH_2$ groups. A shoulder at 2850 cm^{-1} was assignable to vibration of the $-OCH_3$ groups. The band at 1690 cm^{-1} corresponded to conjugated carbonyl groups, whereas two bands at 1605 and 1515 cm^{-1} were characteristic of aromatic rings and were due to vibrations of the aromatic skeleton. Bands at 1460 and 1425 cm^{-1} included a considerable contribution from the C-H bonds of the $-OCH_3$ groups. The Kraft process cleaves β-*O*-4 and α–*O*-4 linkages, leaving a lot of non-etherified phenolic-OH groups in the lignin that are visible in the spectrum at 1365 cm^{-1} (Tejado *et al*., 2007). Syringyl units in lignin molecules were clearly seen at 1330 cm^{-1}, while guaiacyl units appeared as a shoulder at 1270 cm^{-1}. This is in accordance with the results obtained by Ibarra *et al*. (2005), which showed that the lignin in eucalypt wood and pulps is mainly composed of syringyl units with small amount of guaiacyl units (Ibarra *et al*., 2005). Bands at 1155 and 1042 cm^{-1} were characteristic of secondary and primary -OH groups, respectively. A band at 832 cm^{-1} was due

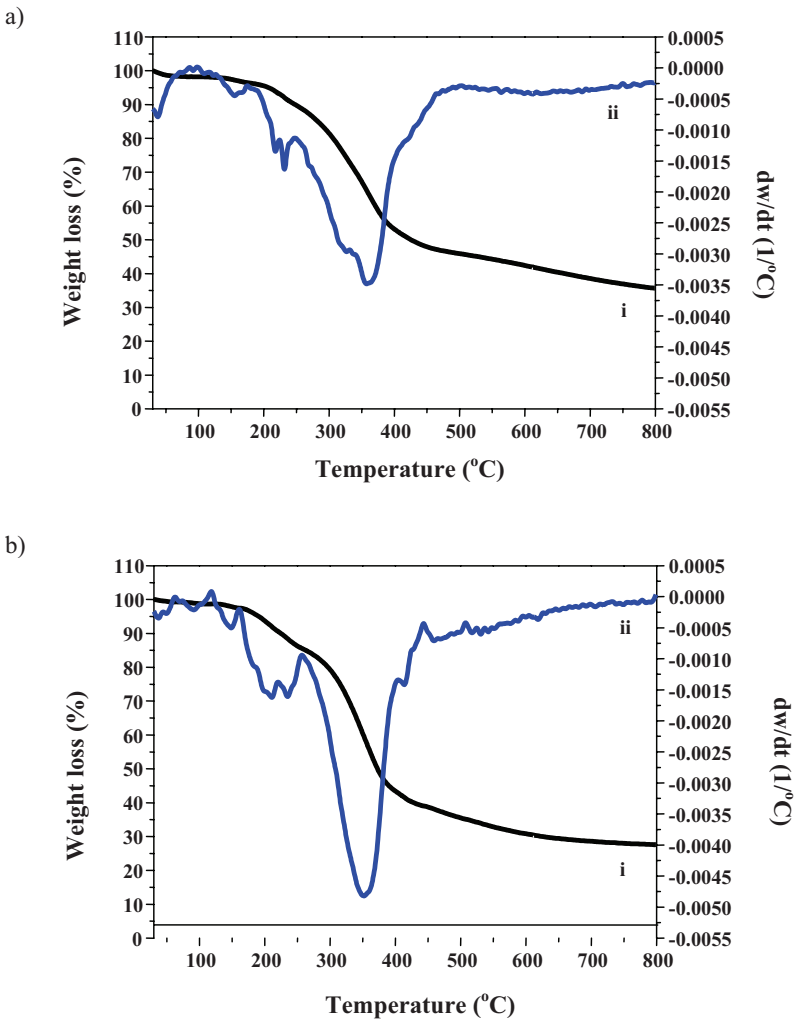

Figure 3 TGA thermograms showing (i) weight loss (ii) derivative of weight loss of lignin; (a) precipitated at pH 4; and (b) extracted with dichloromethane.

to aromatic CH out of plane vibration in a *p*-hydroxy phenylpropane unit of the syringyl units. Due to the scission of ether bonds by the nucleophilic sulfide (S^{2-}) or bisulfide (HS^-) ions, a weak band at 650 cm^{-1} arose from C-S bonds, which is a characteristic of Kraft lignin. All FT-IR results were in agreement with those of numerous previous works (Nada *et al*., 1998; El Mansouri and Salvado, 2007; Tejado *et al*., 2007; Garcia *et al*., 2009; Yuan *et al*., 2009).

Thermal properties

It is well recognised that lignin is thermally more resistant than carbohydrate wood components. The thermal properties of lignin samples were studied by TGA and DSC. TGA curves reveal the weight loss of substances in relation to the temperature of thermal degradation, while the first derivative of that curve shows the corresponding rate of weight loss. The peak of this curve expressed as a thermal decomposition temperature can be used to compare thermal stability characteristics of different materials.

From TGA data shown in Figure 3 and Table 6, all samples showed similar thermal degradation behaviour with T_d (decomposition

Table 5 Assignment of FT-IR absorption of lignin samples.

Wavenumber (cm^{-1})		Assignment
This work	Previous work (Nada *et al*., 1998)	
3390	3440-3430	OH stretching (phenolic OH groups)
2920	2940-2930	CH stretching of methyl or methylene groups
2850	2689-2880	CH vibration of methyl group or methoxyl
1710	1727-1690	C=O stretching (unconjugated C=O)
1690		C=O stretching (conjugated C=O)
1605, 1515	1610-1690, 1505	Aromatic skeleton vibration
1460	1458	CH stretching of methyl or methylene groups
1425	1425-1420	CH vibration of methyl group
1330	1370-1250	Syringyl ring breathing with CO stretching
1270	1260	Guaiacyl ring breathing with CO
1220		C-O(H) stretching of phenolic OH and ether
1155	1160-1140	OH stretching of secondary alcohol
1042	1044	OH stretching of primary alcohol
832	844	Aromatic CH out of plane bending
630	630	CS bonds

Table 6 Thermal properties of lignin samples.

Lignin*	T_d (°C)	T_g (°C)
Precipitated at pH 2	370	134
Precipitated at pH 4	370	134
Extract (1) : dichloromethane	360	79
Extract (2) : acetone	370	133
Extract (3) : methanol	370	140

* corresponding to the lignin samples in Figure 1.

T_d = decomposition temperature at maximum rate.

T_g = glass transition temperature.

temperature) appearing between 360 and 370°C. Nevertheless, it is worth noting that, among all samples, T_d of dichloromethane-soluble lignin was the lowest, indicating the least thermal stability. Furthermore, the thermal stability seemed to be associated with lignin MW. This was well supported by Sun *et al.* (2000), who reported that the thermal stability of lignin increased with increasing MW. T_d of lignin has been found to vary between 300 and 450°C, while hemicelluloses degraded at a temperature range of 200 to 300°C (Sun *et al.*, 2000; Garcia *et al.*, 2009). Pyrolytic degradation of lignin involves fragmentation of inter-unit linkages, releasing monomeric phenol into a vapour phase. The cleavage of methyl-aryl ether bonds is identified at below 400°C, whereas decomposition or condensation of aromatic rings takes place at 400-600°C. After heating to 800°C, all lignin samples remain unvolatized due to the formation of highly condensed aromatic structure (Sun *et al.*, 2000; Tejado *et al.*, 2007).

The glass transition temperature (T_g) values of the lignin samples are shown in Figure 4 and Table 6. Among all samples, T_g of the dichloromethane-soluble lignin was the lowest (about 80°C). Apart from the dichloromethane-soluble lignin, there was no significant difference among the T_g values of the lignin samples. The results associated well with their MW values and were also in agreement with other studies that reported T_g values between 90 and 180°C (Tejado *et al.*, 2007; Garcia *et al.*, 2009).

CONCLUSION

A series of Kraft lignin samples from the black liquor of *Eucalyptus camaldulensis Dehn* were precipitated with concentrated sulphuric acid at various pH levels (2, 4, and 6). It was concluded that there are clear differences between the lignin samples obtained at different pH levels, according to their yields and ash content. The precipitation

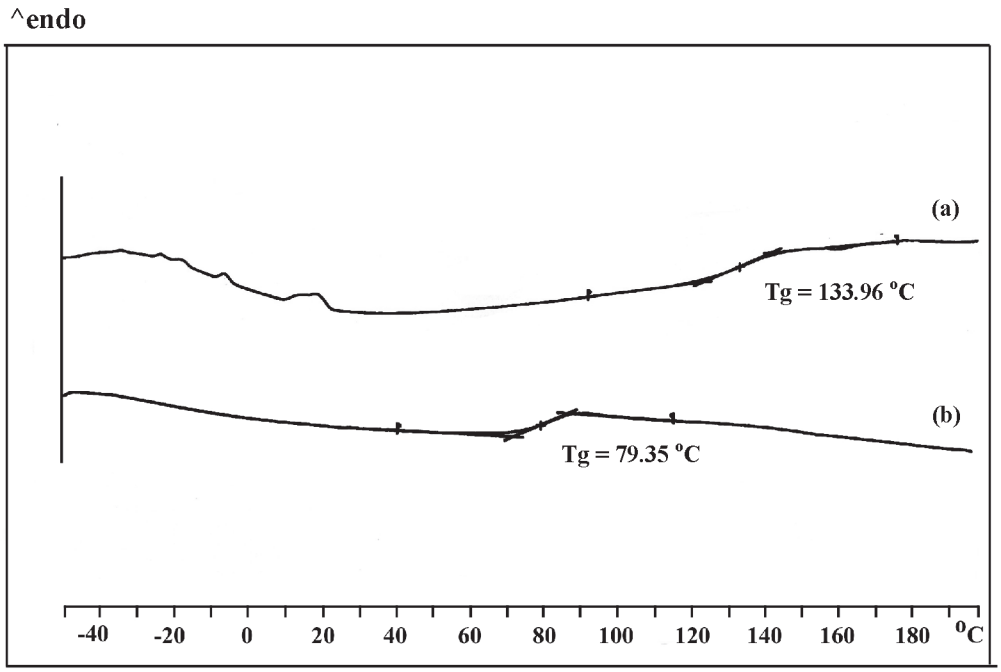

Figure 4 DSC thermograms of the lignin samples (a) lignin precipitated at pH 4; and (b) lignin extracted with dichloromethane.

at pH 4 gave the highest yield and the lignin obtained exhibited similar properties to that precipitated at pH 2. Selective extractions for low MW lignin were further performed on the lignin obtained, using various organic solvents (dichloromethane, acetone and methanol). The low MW lignin samples extracted from acetone and methanol possessed the same properties as the starting lignin. In contrast, extraction with dichloromethane produced lignin with a lower molecular weight (about 940 g mol^{-1}), leading to lower T_d (about 360°C) and T_g (about 80°C).

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