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ARTICLE TYPE

# Water soluble kraft lignin-acrylic acid copolymer: synthesis and characterization

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Lignin produced in the kraft pulping process is insoluble in water at neutral pH, which limits its application in industry. In this paper, kraft lignin (KL) was copolymerized with acrylic acid (AA) in an aqueous solution to produce a water soluble lignin-based copolymer. The copolymerization was carried out using  $K_2S_2O_8$ - $Na_2S_2O_3$  as the initiator under alkaline aqueous conditions, and the influence of the reaction parameters, i.e. initiator dosage, reaction time and temperature, mole ratio of acrylic acid to lignin and reaction concentration, on resultant lignin copolymers were investigated. The mechanism of copolymerization of kraft lignin with acrylic acid was also discussed in this work. The resultant lignin copolymer was characterized by Fourier Transform Infrared (FTIR) spectrophotometry and Nuclear Magnetic Resonance (NMR). The successful copolymerization of AA and KL was confirmed by the new absorption peak of carboxyl anions in the FTIR spectrum and new peaks in the  $^1H$ -NMR spectrum. At optimal conditions, the charge density and molecular weight of lignin copolymer reached 1.86 meq/g and 46,421 g/mol, respectively, and the solubility of lignin after reaction was increased from 1.80 g/L to 100 g/L at neutral pH.

## 1. Introduction

Lignin is a three-dimensional aromatic polymer and the second most abundant bio-polymer after cellulose on earth. It is estimated that over 50 million tons of lignin is produced in the pulp and paper industry annually.<sup>1,2</sup> Currently, the majority of kraft lignin is burned as fuel.<sup>2,3</sup> Various types of lignin products were available in the market since 1940s. For example, Mead soda lignin and MeadWestvaco kraft lignin have been produced in the US since 1940s, kraft lignin and lignosulfonate were also produced in Canada and Sweden for many years.<sup>4</sup> The current main producer of sulfonated and unsulfonated soda lignin is ALM Ltd. in India.<sup>2, 5</sup> Recently, commercial kraft lignin production plants have been developed by WestFraser company in Alberta, Canada, using LignoForce technology<sup>6</sup> and by Domtar using LignoBoost technology in North Carolina, USA.<sup>7</sup> However, other value-added products can be generated from lignin in the general context of forest biorefinery.<sup>8,9</sup> In the past, the application of lignin in producing phenol<sup>10</sup>, liquid fuels<sup>11</sup>, activated carbon<sup>12</sup> and carbon fiber<sup>13</sup> were investigated. Alternatively, lignin can be modified and used as a surfactant in various applications including a binder, additive in oil drilling, dispersant for coal-water slurry, water reducing agent for cement and a scale inhibitor for recirculating cooling water system.<sup>14-18</sup> Current research on producing lignin-based value-added products is mainly focused on lignosulfonate due to its high water solubility over a wide pH range.<sup>19-21</sup> The limited production and impurity of lignosulfonate as well as the need for lignin with a high purity and large production generated incentives for the production of kraft lignin.<sup>22, 23</sup> Kraft lignin

(KL), which is obtained from the black liquor of kraft pulping process via acidification, is currently the majority of lignin produced in pulping and papermaking industry.<sup>24</sup> Unlike lignosulfonate produced from a sulfite pulping process, kraft lignin is only soluble in alkaline solutions, which hinders its application in industry,<sup>25, 26</sup> but it can be modified in order to overcome these difficulties.

Various investigations have been conducted on lignin in order to produce new products with beneficial properties. Pang et al. oxidized calcium lignosulfonate using hydrogen peroxide under alkaline conditions to produce cement dispersants, and the dispersibility of oxidized calcium lignosulfonate increased by 34.2%.<sup>27</sup> Ouyang et al. carried out the hydroxymethylation and sulfonation of alkali lignin, which increased its dispersibility in cement pastes by 85%.<sup>27, 28</sup> He and Fatehi sulfomethylated kraft lignin to produce dispersant for cement admixture.<sup>29</sup> Aso et al. modified kraft lignin using polyethylene glycol diglycidylether, ethoxy (2-hydroxy) propoxy polyethylene glycol glycidylether, and dodecyloxy-polyethylene glycol glycidyl ether in order to prepare the lignin-based amphiphiles for cement dispersant.<sup>25,26,30</sup>

Nevertheless, the molecular weight and number of functional group of lignin play an important role on its end-use application, and it was reported that the low molecular weight and relatively small number of functional groups on modified kraft lignin suppressed its application as a dispersant for cement.<sup>27, 30</sup> It was reported that the dispersibility of calcium lignosulfonate was decreased by 40 % with the decrease in the molecular weight from 30,000 g/mol to 1,000 g/mol.<sup>31</sup> Overcoming these challenges, the copolymerization of lignin with vinyl monomers is a promising method, which can increase both the molecular

weight and number of functional groups attached to lignin.

A number of studies have been carried out on the copolymerization of lignosulfonate or lignin with various vinyl monomers<sup>32-37</sup>. The copolymerization reaction can be initiated by chemo-enzymatic starters, UV radiation, Fe(II)/Ca(II)-H<sub>2</sub>O<sub>2</sub> system, ceric ammonium nitrate and persulfate in aqueous or organic solvents.<sup>32-35, 38</sup> In this context, we have carried out the copolymerization of kraft lignin with acrylic acid in alkaline aqueous solution using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> as an initiator. The first objective of this work was to investigate the changes in the properties of kraft lignin after copolymerization. The second objective of this study was to produce water soluble kraft lignin copolymer by conducting the reaction in an alkaline aqueous solution, which would facilitate the direct use of black liquor to produce lignin copolymer. The main novelty of this work is that the copolymerization mechanism of kraft lignin with acrylic acid was investigated in details. This study also intends to report how the properties of softwood kraft lignin will be affected by this modification for end-use applications. It should be stated that a kraft lignin-acrylic acid based copolymer 1) is green as it contains lignin (i.e. wood component), 2) can replace oil-based dispersants and flocculants that are currently used in industry, and 3) is inexpensive and can be readily produced in large scales.

## 2. Experimental

### 2.1. Materials

Softwood kraft lignin sample (KL) was received from FPIInnovations from its pilot plant facilities in Thunder Bay, ON. The kraft lignin was produced via LignoForce™ technology.<sup>6</sup> Acrylic acid (AA), polydiallyldimethylammonium chloride (PDADMAC, 100,000-200,000 g/mol), sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) (analytical grades), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) (analytical grades), dimethyl sulphate, pyridine, acetic anhydride, para-hydroxybenzoic acid, 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane, chromium(III) acetylacetonate, Deuteriochloroform (CDCl<sub>3</sub>), anhydrous pyridine, sodium hydroxide (97%, reagent grade), hydrochloric acid (37%, reagent grade) and poly(acrylic acid) with 15,000 g/mol were obtained from Sigma-Aldrich Company, and used as received. Dialysis membrane (Cut off of 1000 g/mol) was obtained from SpectrumLabs. 1,3-didecyl-2-methylimidazolium chloride (DDMCI, TEGO trant A 100) was supplied by Metrohm Company.

### 2.2. Acetylation of KL

To understand if the copolymerization of KL with AA happens in the absence of phenolic and aliphatic hydroxyl groups, the KL was acetylated using the method described by Andes et al.<sup>39</sup> A 0.5 g sample of KL was dissolved in 6 mL of pyridine-acetic anhydride (1:1, v/v) by stirring for 30 min at 300 rpm, 25 °C and then kept in the dark at room temperature for 72 h. The solution was then added dropwise to 120 mL of ice-cold water and then centrifuged/washed 3 times. The solvent was removed from the sample using a freeze dryer and the final product was denoted as acetylated KL.

### 2.3. Methylation of KL

To find out if the lignin radicals driven from phenolic hydroxyl group participated in the copolymerization with AA, the KL was methylated according to the method used by Sadeghifar et al.<sup>40</sup> A 2.0 g sample of KL was dissolved in 30 mL of 0.7 mol/L NaOH solution at room temperature by stirring at 200 rpm for 30 min. In a glass beaker, a 2.5 mmol of dimethyl sulphate was added per each mmol of total phenolic hydroxyl groups of

lignin, and the solution was stirred at room temperature for 30 min. The mixture was then heated to 80 °C for 2 h. During the reaction, the pH of the mixture was maintained at 11-11.5 by continuous addition of 0.7 mol/L NaOH solution. After the reaction, the mixture was acidified to pH 2.5 by adding 2 mol/L HCl solution and the solid precipitate was washed with excess amount of deionized water until neutral pH was obtained and the sample was then freeze-dried. The final product was denoted as methylated KL.

### 2.4. H<sub>2</sub>O<sub>2</sub> treatment of KL

In order to understand the reaction mechanism of lignin with AA, hydrogen peroxide was used to treat kraft lignin in order to remove the carbonyl structure existing on kraft lignin. The reaction conditions were fixed at 0.2 mol/L kraft lignin concentration, 0.05 mol/L peroxide concentration, 70 °C, 2 h and pH 10.5. After the reaction, the solution was neutralized using 1.0 mol/L H<sub>2</sub>SO<sub>4</sub> and dialyzed for 48 h using the aforementioned membrane. The sample collected from the membrane was dried at 60 °C and considered as H<sub>2</sub>O<sub>2</sub>-treated KL in this study.

### 2.5. Copolymerization of AA and KL

The copolymerization reactions were carried out under a nitrogen atmosphere in a 250 mL three-necked round bottom flask equipped with a magnetic stirrer. A 2.0 g of KL was dissolved in 50 mL of 1.0 % sodium hydroxide solution at a specific temperature stirring at 280 rpm, the solution was then placed into three neck flasks and purged with nitrogen for 15 min. The flask was then charged with the predetermined amount of initiator (2/1 K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> mass ratio). After 10 min of stirring, different amounts of AA were added into the flask and the final pH of the solution was adjusted to 10.2 ± 0.2 to keep lignin dissolved in the reaction solution. A continuous supply of nitrogen was maintained throughout the reaction. The copolymerization reaction was repeated at different temperatures (40 °C, 50 °C, 60 °C, 70 °C and 80 °C), times (0.5 h, 1 h, 2 h, 3 h and 4 h), initiator dosages (0.5 wt.%, 1.0 wt.%, 1.5 wt.%, 2.0 wt.% and 3.0 wt.%, based on lignin mass), AA to lignin mole ratios (1.35, 2.70, 5.4, 8.0, 10 and 13.5) and reaction concentrations (0.07 mol/L, 0.1 mol/L, 0.13 mol/L, 0.2 mol/L and 0.35 mol/L) in order to optimize the reaction conditions.

### 2.6. Purifying KL-AA copolymer

Upon completion, the temperature of the solution was cooled to room temperature by immersing the flask in water for 20 min. The pH of the reaction solution was then adjusted to 2.0 by the addition sulfuric acid and water to make final volume at 100 mL with stirring the reaction medium for 30 min. This resulted in the precipitation of KL-AA copolymer. The suspension was centrifuged at 4000 rpm for 10 min in order to collect the precipitated copolymer and remove the homopolymer (poly acrylic acid, PAA) and unreacted AA. Ultra violet spectroscopy Genesys 10s UV-Vis spectrophotometer (Thermo Scientific, Madison, USA), 280 nm, was used to measure the amount of lignin copolymer that is left in the acidic supernatants of PAA homopolymer and AA. PAA and AA were stated to be water soluble even at pH 1.5.<sup>41</sup> The acidic solubility of PAA and AA was also confirmed in our experiment by dissolving 30 g of commercial PAA (C-PAA) (with the molecular weight of 15,000 g/mol) and the PAA (H-PAA) that was prepared in the current study (with the molecular weight of 6,900 g/mol), in 100 mL water solution at pH 2.0 and room temperature for 20 min. The C-PAA and H-PAA were mixed, separately, with KL without reaction, and then separated through the

acidification/centrifugation process. After 3 cycles of acidification/centrifugation, there was no C-PAA or PAA in the KL precipitates, which was confirmed by H-NMR analysis implying that the acidification/centrifugation process was effective in separating lignin-AA copolymer from PAA or unreacted AA. Subsequently, the precipitated KL-AA copolymers were added to 100 mL of deionized water and the pH of the solution was adjusted to  $7.0 \pm 0.2$ . The samples were purified using dialysis membranes for 48 h in order to remove any remaining impurities (e.g. inorganic salt induced by pH adjustment) from the copolymer. The deionized water used for dialysis was changed once every 6 h. After dialysis, the solution was dried at  $60\text{ }^\circ\text{C}$ , and the dried sample was considered as the final lignin copolymer product (LCP).

### 2.7. Copolymerization of treated lignins with AA

In this set of experiments, the methylated KL, acetylated KL,  $\text{H}_2\text{O}_2$ -treated KL and untreated KL were copolymerized with acrylic acid at fixed conditions of 0.35 mol/L lignin, AA/lignin ratio of 8.0 mol/mol, 1.5 wt.% initiator (based on lignin mass),  $70\text{ }^\circ\text{C}$ , 3 h and pH  $10.2 \pm 0.2$ . Upon completion, the lignin-based product was separated from the reaction mixture following the procedure stated in section 2.6. The final dialyzed samples were dried in an oven at  $60\text{ }^\circ\text{C}$ .

### 2.8. Preparation of homopolymerized PAA (H-PAA)

The H-PAA was prepared under the same procedure as stated in Section 2.5. The conditions were fixed at 2.8 mol/L AA,  $70\text{ }^\circ\text{C}$  0.47 wt.% initiator, 3 h and pH  $10.2 \pm 0.2$ , which is same as the optimal conditions of copolymerization of KL and AA, 0.35 mol/L KL, AA/KL ratio of 8.0 mol/mol, 1.5 wt.% initiator, 3 h and  $70\text{ }^\circ\text{C}$  without the presence of KL. After the reaction, the solution was neutralized using 0.1 mol/L sulfuric acid and put into the membrane tubes to dialyze for 48 h in order to remove the remaining impurities (e.g. inorganic salt induced by pH adjustment) and unreacted AA from the PAA. The deionized water used for dialysis was changed once every 6 h. After dialysis, the solution was dried at  $60\text{ }^\circ\text{C}$ , and the dried sample was considered as homopolymerized PAA (H-PAA).

### 2.9. S-PAA production

In this set of experiments, the copolymerization of KL and AA was carried out under the optimal conditions of 0.35 mol/L KL, AA/KL ratio of 8.0 mol/mol, 1.5 wt.% initiator, 3 h and  $70\text{ }^\circ\text{C}$ . Upon completion of reaction, the solution was treated according to the procedure stated in section 2.6. The supernatant of this separation process, which contained PAA and AA, was collected and neutralized using sodium hydroxide, and then dialyzed for 48 h to remove the unreacted AA and inorganic salt as stated in section 2.6. Then, the sample was dried at  $60\text{ }^\circ\text{C}$ , and the dried sample was considered as separated PAA (S-PAA).

### 2.10. Reaction of KL and PAA

To understand if there is esterification reaction between lignin and PAA, the C-PAA and H-PAA was reacted with KL separately under the conditions of 0.35 mol/L of lignin, 8.0 mol/mol of PAA/KL, 1.5 % initiator,  $70\text{ }^\circ\text{C}$ , 3 h and pH  $10.2 \pm 0.2$ . After the reaction, the solution was treated using the same procedure stated in section 2.6 and the final product was analysed by H-NMR.

### 2.11. Reaction conversion analysis

The weight of PAA ( $W_{\text{PAA}}$ ), and the weight of LCP and PAA ( $W_{(\text{LCP}+\text{PAA})}$ ), which was collected from the membrane dialysis,

was used to calculate the AA conversion ratio according to the equation developed by Chen et al.<sup>42</sup>

In the copolymerization system:

$$\text{AA conversion ratio (\%)} = 100 \times \frac{W_{(\text{LCP}+\text{PAA})} - W_{\text{KL}}}{W_{\text{AA}}} \quad (1)$$

In homopolymerization system:

$$\text{AA conversion ratio (\%)} = 100 \times \frac{W_{\text{PAA}}}{W_{\text{AA}}} \quad (2)$$

where  $W_{\text{AA}}$  is the amount of AA used in the experiment and  $W_{\text{KL}}$  is the amount of lignin used in the experiments.

### 2.12. Charge density and carboxylic group analyses

A 0.10 g of dried LCP was added to 100 mL of deionized water to generate a suspension in a 125 mL Erlenmeyer flask. The suspension was immersed into a water bath shaker (Innova 3100, Brunswick Scientific, Edison, NJ, USA) and shaken (100 rpm) at  $30\text{ }^\circ\text{C}$  for 1 h. The suspension was then centrifuged at 1000 rpm for 5 min. The supernatant was collected and used to analyse the charge density and carboxyl group content of soluble LCP. The concentration of LCP in supernatant was determined by drying the supernatant at  $105\text{ }^\circ\text{C}$ .

The charge density of dissolved LCP was measured by a particle charge detector, Mütek PCD 04 titrator (Arzbergerstrae, Herrsching, Germany) with PDADMAC solution (0.0050 mol/L). The reported data in this paper is the average of three repetitions.

The carboxyl group of KL and LCP was measured using an automatic potentiometric titrator (T905 potential Titrand, Metrohm Corp. Switzerland). The Ag/AgCl electrode was used as reference electrode and the ionic surfactant electrode was used as a working electrode. The sample dissolved at pH 10 buffer solution was titrated against 0.0040 mol/L TEGO trant A 100 solution. The amount of carboxyl group was used to calculate the grafting ratio according to the equation described by Bayazeed et al.<sup>45</sup>

$$\text{Grafting ratio (\%)} = \frac{100 \times C \text{ mol/g} \times 94 \text{ g/mol}}{1 - C \text{ mol/g} \times 94 \text{ g/mol}} \quad (3)$$

where C is the concentration of carboxyl group in LCP, mol/g. 94 g/mol is the molecular weight of acrylic acid sodium unit.

### 2.13. Phenolic hydroxyl group analysis

The phenolic hydroxyl content of KL and LCP were measured using an automatic potentiometric titrator (785 DMP Titrimo, Metrohm, Switzerland). About 0.06 g sample of dried KL or LCP was added to 100 mL of deionized water containing 1 mL of 0.8 mol/L potassium hydroxide in a 250 mL beaker. After stirring at 200 rpm for 5 min, 4 mL of 0.5 % para-hydroxybenzoic acid solution was added as an internal standard, and the solution was titrated by 0.1 mol/L hydrochloric acid. During the titration, with the decrease in the pH of the sample solution, the first two endpoints appeared in sequence were noted as  $V_1'$  and  $V_2'$ , respectively. The corresponding two endpoints in the titration curve of blank sample were specified as  $V_1$  and  $V_2$ , respectively. The phenolic hydroxyl group content of samples were calculated according to equation (4), which was claimed by Zhou et al.<sup>44</sup> The reported data in this paper is the average of three repetitions.

$$\text{phenolic hydroxyl group content} \left( \frac{\text{mmol}}{\text{g}} \right) = \frac{C_{\text{HCl}} \left[ (V_2' - V_1') - (V_2 - V_1) \right]}{m} \quad (4)$$

$C_{\text{HCl}}$  is the concentration of HCl solution as titrant, 0.1 mmol/L. m is the mass (g) of the sample.  $V_1$  and  $V_2$  are the volumes (mL) of HCl solution used for the two endpoints in blank titration.  $V_1'$

and  $V_2'$  are the volumes (mL) of HCl solution, used for the two endpoints in sample titration, respectively.

#### 2.14. Hydrodynamic diameter measurement of KL and LCP in aqueous solutions

The hydrodynamic diameter of the KL and LCP segments were measured using a dynamic light scattering analyzer (type BI-200SM Brookhaven Instruments Corp., USA). The light source is a power solid state laser with a maximum power of 35 mW and a wavelength of 637 nm. The experimental procedure was adopted as described by Yan et al.<sup>45</sup> The KL and LCP were dissolved in aqueous solution at pH 11.0. The obtained solution was stirred for 30 min at 300 rpm, 25 °C and allowed to set for 24 h to reach equilibrium. A sample solution of 20 mL was prepared by filtration with a 0.22 µm disposable syringe filter and kept in a glass bottle. Each test was measured for 2 min, and five measurements were performed for each sample and the mean value was used. The sample was kept under isothermal conditions at 25±0.02 °C. The scattering angle was set at 90 °.

#### 2.15. Molecular weight analysis

A 100 mg sample of air dried KL was initially suspended in 4.0 mL of acetic anhydride/pyridine 1:1 (V:V) solution stirring for 30 min at 300 rpm, 25 °C and then kept in the dark at 25 °C for 24 h. The resulting solution was then poured into an excess (50 ml) of ice water and centrifuged/washed 3 times. The solvent was removed from the sample using a freeze dryer. The acetylated KL were dissolved in 10 mL of tetrahydrofuran (THF) by 300 rpm stirring for 30 min at room temperature and then filtered with a PTFE filter (13 mm diameter and 0.2 µm pore size). The filtered samples were used for molecular weight analysis. For LCP analysis, a 50 mg of air dried LCP sample was dissolved in 10 mL of 0.1 mol/L NaNO<sub>3</sub> solution and filtered with a nylon 0.2 µm filter (13 mm diameter). The filtered solutions were used for molecular weight analysis.

The molecular weight analysis of the samples was carried out using a gel permeation chromatography, Malvern GPCmax VE2001 Module + Viscotek TDA305 with multi-detectors (UV, RI, viscometer, low angle and right angle laser detectors). For KL measurement, the organic columns of PolyAnalytic PAS106M, PAS103 and PAS102.5 were used, and HPLC-grade tetrahydrofuran (THF) was used as solvent and eluent. The flow rate was set at 1.0 mL/min. For LCP measurement, the columns of PolyAnalytic PAA206 and PAA203 were used, and 0.1 mol/L NaNO<sub>3</sub> solution was used as solvent and eluent. The flow rate was set at 0.70 mL/min. The column temperature was set at 35 °C for both systems. Polystyrene polymers were used as standards for organic system and poly (ethylene oxide) for the aqueous system.

#### 2.16. Fourier Transform Infrared (FTIR)

The Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted on KL, LCP and PAA. The samples were firstly dried in oven at 105 °C overnight and 0.05 g of the samples was used for analysis using FTIR (Bruker Tensor 37, Germany, ATR accessory). The spectra were recorded in transmittance mode in the range 600 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> with 4 cm<sup>-1</sup> resolution, and 32 scans per sample were conducted.

#### 2.17. <sup>1</sup>H-NMR analysis

The acetylated KL-AA copolymer, methylated KL-AA copolymer, KL, the product of KL and PAA copolymerization, LCP and H-PAA were analyzed by <sup>1</sup>H-NMR spectroscopy. Samples of dried KL, LCP and PAA were dissolved in D<sub>2</sub>O or DMSO-*d*<sub>6</sub> at 40-50 g/L concentration. The solution was stirred

for 30 min to fully dissolve the material. The NMR spectra of these samples were recorded using an INOVA-500 MHz instrument (Varian, USA) with a 45° pulse and relaxation delay time of 1.0 s.

#### 2.18. <sup>31</sup>P-NMR analysis

The success of acetylation and methylation of KL were determined by quantitative <sup>31</sup>P-NMR using previously established procedures.<sup>46</sup> A 35-45 mg of dried sample was dissolved in 500 µL of anhydrous pyridine/CDCl<sub>3</sub> mixture (1.6:1, v/v). Cyclohexanol (200 µL, 21.48 mg/mL) was added as the internal standard and 50 µL of a chromium (III) acetylacetonate solution (5.6 mg/mL) was added to the pyridine/CDCl<sub>3</sub> solution as the relaxation reagent. Finally, 100 µL of phosphitylating reagent II (2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane) was added and transferred into a 5 mm NMR tube for NMR acquisition. The NMR spectra of these samples were recorded using an INOVA-500 MHz instrument (Varian, USA) with a Quad probe dedicated to <sup>31</sup>P.

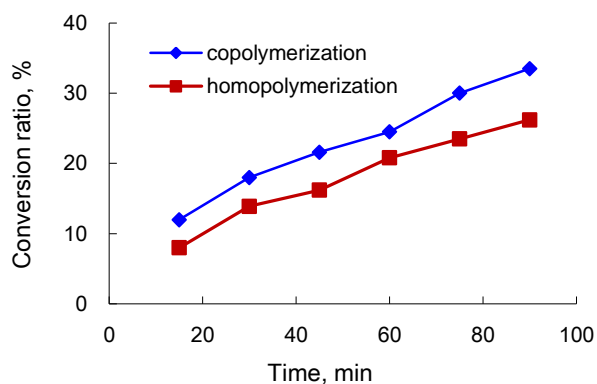
#### 2.19. Solubility analysis of KL and LCP

The solubility of KL and LCP was determined based on the method described by Lappan et al.<sup>47</sup> A 5.0 g sample of KL or LCP was added to 50 mL of deionized water at different pHs using 1.0 mol/L NaOH or 1.0 mol/L H<sub>2</sub>SO<sub>4</sub> solution in a 125 mL Erlenmeyer flask. The suspension was immersed into a water bath shaker (Innova 3100, Brunswick Scientific, Edison, NJ, USA) and shaken (100 rpm) at 30 °C for 1 h. The suspension was then centrifuged at 1000 rpm for 5 min. The concentration of KP or LCP in the supernatants was determined by drying the supernatant at 105 °C to determine the solubility of KL or LCP, the mass of NaOH or H<sub>2</sub>SO<sub>4</sub> added for adjusting the pH was taken into account.

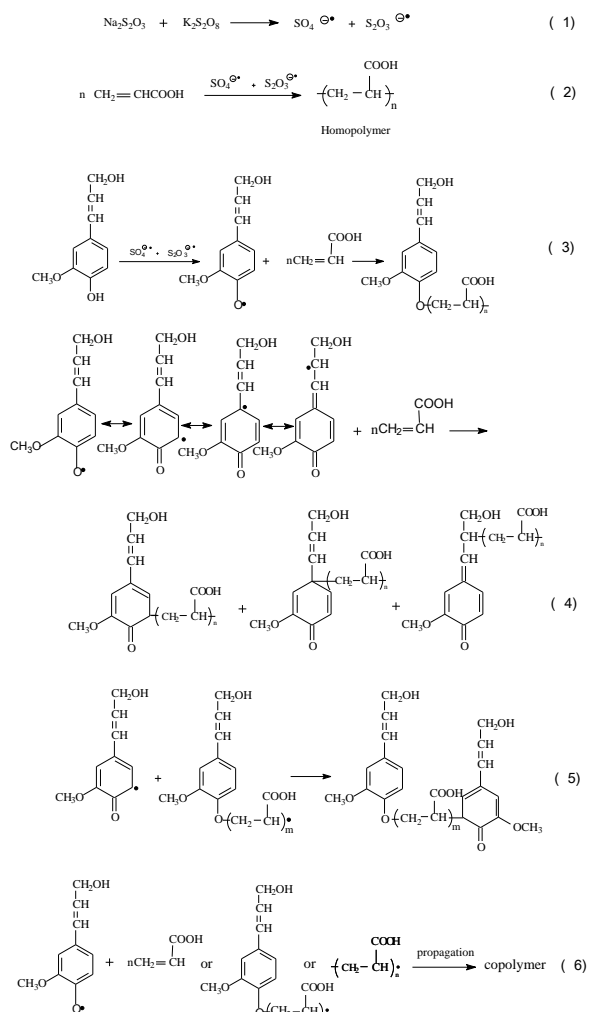
### 3. Results and discussion

#### 3.1. Mechanism of copolymerization of KL with AA

There are two contradictory opinions on the role of lignin played in its copolymerization with vinyl monomers such as acrylic acid, or acrylamide, in the literatures: 1) the addition of lignin accelerates the polymerization of the monomers due to the existence of phenolic groups that could act as an active site in the polymerization.<sup>48, 49</sup> and 2) lignin with its macromolecular structure might inhibit the polymerization of vinyl monomers.<sup>50, 51</sup> Past investigations about the copolymerization of lignosulfonate with vinyl monomers have demonstrated that the existence of either hardwood or softwood lignosulfonate in the copolymerization system could improve the monomer conversion, and the lignosulfonate participated in the copolymerization at the beginning of reaction.<sup>52</sup> In order to understand the role of KL in the copolymerization with AA, the conversion ratio of AA in the homopolymerization system that produces H-PAA and in the copolymerization system that produces LCP were determined and presented in Fig. 1.



**Fig. 1.** Conversion ratio of AA in LCP and H-PAA productions as a function of reaction time

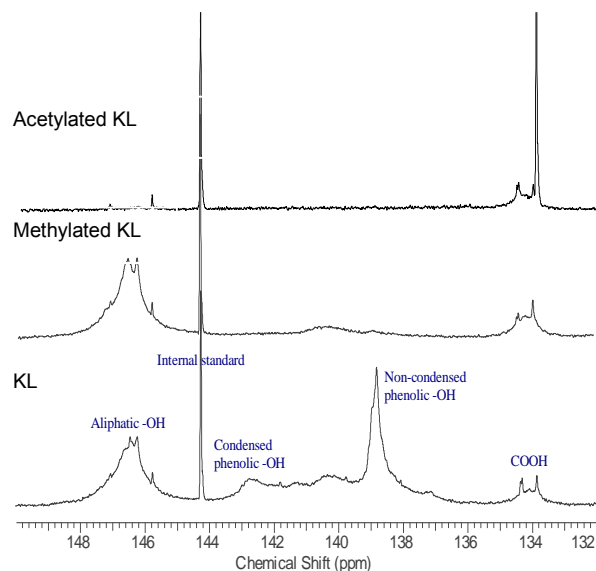


**Fig. 2.** Proposed reaction mechanism of copolymerization of AA with KL

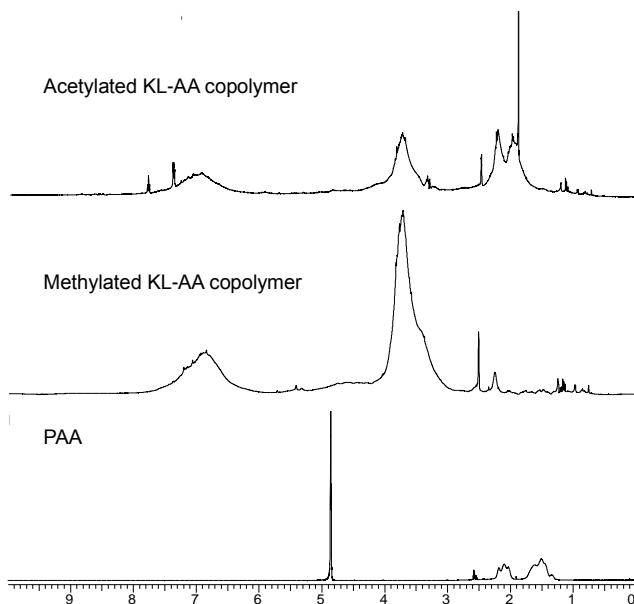
As illustrated in Fig. 1, the conversion ratio of AA in LCP production system was higher than that in the H-PAA production system over the time studied. The maximum conversion ratio was 33.5 % for LCP copolymerization at 90 °C, and 26.2 % for PAA homopolymerization, which demonstrated that the presence of kraft lignin accelerated the conversion rate of acrylic acid monomer (AA). We can conclude that KL accelerated the copolymerization. Similar results were obtained

in the copolymerization of acrylonitrile and methyl methacrylate with liginosulfonate derived from pine<sup>49</sup> as well as the copolymerization of kraft lignin and styrene.<sup>53</sup>

Figure 2 shows the proposed copolymerization scheme of KL and AA. Softwood KL is guaiacyl lignin, which is composed principally of coniferyl alcohol units.<sup>54</sup> Hence, the coniferyl alcohol was chosen to represent KL in this figure. During the copolymerization reaction, the sulfate radicals are initially formed by the redox reaction between  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{Na}_2\text{S}_2\text{O}_3$  (reaction (1)), which is able to initiate the homopolymerization of vinyl monomers (reaction (2)).<sup>44,49</sup> Also, the sulfate radicals



**Fig. 3.** <sup>31</sup>P-NMR spectra of acetylated KL, methylated KL and KL



**Fig. 4.** <sup>1</sup>H-NMR spectra of acetylated KL-AA copolymer, methylated KL-AA copolymer and PAA (H-PAA)

can take the unstable hydrogen from phenol group of KL to generate phenoxyl radical (reaction (3)), which can propagate the copolymerization reaction (reaction (3)).<sup>52</sup>

In addition, the phenoxyl radical can form its resonance forms such as  $\text{C}_5$  radical,  $\text{C}_1$  radical and  $\text{C}_\beta$  radical,<sup>55</sup> which can participate in the copolymerization reaction (reaction (4)) and in

a radical coupling termination reaction with either propagating monomers or the lignin polymer macromolecules chain (reaction 5).<sup>44,50</sup> During these reactions, lignin may play a role of chain transfer agent as reported in the literature,<sup>53</sup> which may affect the molecular weight of PAA formed in this copolymerization system. To clarify this, the molecular weight and the molecular weight distributions of H-PAA and S-PAA were determined. It was found that S-PAA had  $M_n$  and  $M_w$  of 4380 and 5700 g/mol, while H-PAA had  $M_n$  and  $M_w$  of 5050 and 6900 g/mol, respectively. Therefore, KL terminated the polymer radicals in this copolymerization system illustrating that KL indeed acted as a chain transfer agent.

As there are abundance of hydroxyl groups derived from phenolic and aliphatic hydroxyl groups on lignin, PAA may graft on kraft lignin via esterification reaction. To assess this, the reaction of KL and H-PAA was carried out in the presence of the initiator and the final product was analyzed using H-NMR. The H-NMR spectrum of the product provided no evidence for the presence of PAA chain in the product, implying that H-PAA did not graft on lignin. Therefore, the esterification reaction between KL and PAA did not happen in the KL-AA reaction system. As reported in the literature,<sup>54,55</sup> kraft lignin is a very complex material and includes different structures such as alpha-carbonyl (conjugated ~10%), stilbene (~5%) and vinyl ether (~3-4%), which might affect the copolymerization due to the conjugated double bond structure in lignin units. Figure 3 shows that <sup>31</sup>P-NMR spectra of KL, acetylated KL and methylated KL. To determine if other functional groups present in lignin affect the copolymerization, KL was acetylated, which protected the phenolic and aliphatic hydroxyl groups of lignin without impacting the other parts of lignin structure<sup>56</sup>, as shown in Figure 3, and then reacted with AA. The <sup>1</sup>H-NMR spectra of the product were shown in Figure 4. The peak of PAA was not observed in the final product in Figure 4, implying that AA was not grafted onto lignin in the absence of phenolic and aliphatic hydroxyl groups in lignin structure. Also, it illustrated that the double bond containing structures of lignin units that excluded phenolic and aliphatic hydroxyl groups did not affect the copolymerization of KL with AA.

In this copolymerization, lignin radicals mainly derived from the phenolic hydroxyl groups due to the high stability of phenoxy radicals and the low stability of aliphatic alcohol radicals, which might form in this reaction.<sup>57</sup> To attest that the lignin radicals derived from the phenolic hydroxyl groups in this reaction, the KL was first methylated using dimethyl sulphate in order to selectively protect the phenolic hydroxyl groups of KL<sup>40</sup>, as shown in Figure 3. In this case, the aliphatic hydroxyl groups are accessible for reaction with AA. The methylated KL was reacted with AA, and upon examination of the <sup>1</sup>H-NMR (Figure 4), no PAA peak was present in the spectrum, demonstrating i) the AA was not able to graft onto lignin in the absence of phenolic hydroxyl group in lignin units. ii) the existence of aliphatic hydroxyl groups of KL didn't facilitate the grafting of AA on KL. In addition, the phenolic hydroxyl group content of KL decreased from the original amount of 1.73 mmol/g to 0.87 mmol/g after copolymerization, which demonstrated that the phenolic hydroxyl group of KL participated in the reaction.

To investigate if the resonance forms of phenoxy radicals, such as C<sub>5</sub> radicals, C<sub>1</sub> radicals and C<sub>β</sub> radicals (Figure 2, reaction 4) also participate in the reaction, hydrogen peroxide was used to remove any existing carbonyl group from KL based on the

method established previously.<sup>58</sup> Figure 5 shows the FTIR spectra of KL and hydrogen peroxide treated KL. An absorption peak at 1710 cm<sup>-1</sup>, which is assigned to the carbonyl group of lignin, was very weak on the treated KL, but was very strong on untreated KL, providing evidence that the hydrogen peroxide treatment was successful in removing carbonyl structure from untreated KL.

The FTIR spectra of LCPs, which were produced from H<sub>2</sub>O<sub>2</sub> treated and untreated KLs, were presented in Figure 6. The LCPs produced from both KLs contained the carbonyl group (peak at 1710 cm<sup>-1</sup>). Therefore, it is inferred from the results in Fig. 5 and 6 that the resonance forms of phenoxy radicals are produced and involved in the copolymerization reactions shown in Figure 2. A similar behaviour was reported in the copolymerization of softwood lignosulfonate with acrylic acid.<sup>32</sup> Therefore, lignin phenoxy radical can react with monomers, propagated monomer macromolecules or other lignin monomer macromolecules, and finally form LCP copolymer (reaction (6)). During this copolymerization process, the carboxylic acid groups from the monomers (acrylic acid) are introduced onto the LCP molecules, which increase the water solubility, charge density, and the molecule weight of the resulting LCP copolymer.

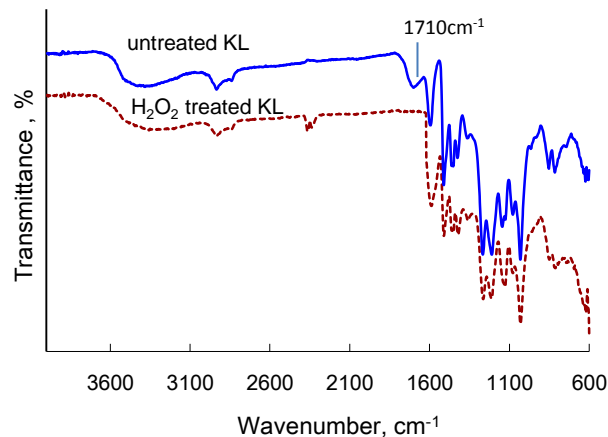


Fig. 5. The FTIR spectra of untreated and H<sub>2</sub>O<sub>2</sub> treated KLs.

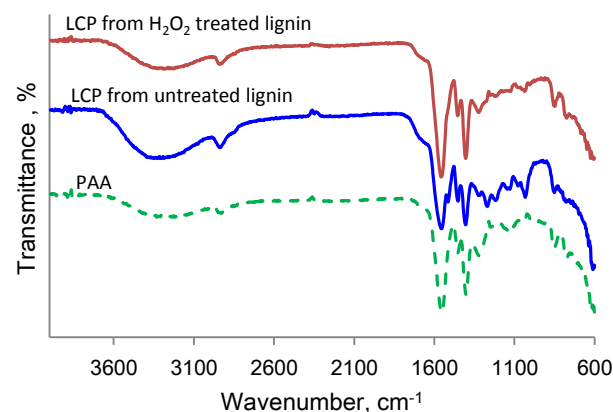
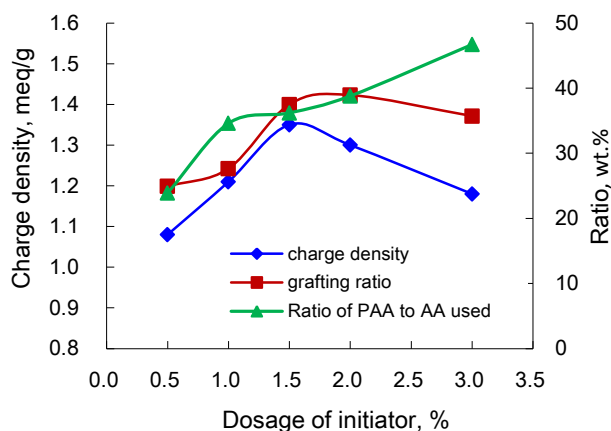


Fig. 6. The FTIR spectra of PAA (H-PAA) and LCPs from untreated and H<sub>2</sub>O<sub>2</sub> treated KLs.

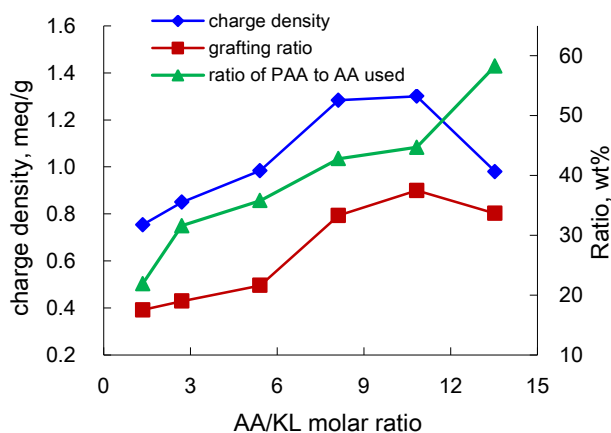
### 3.2. The effects of reaction conditions on the copolymerization

**3.2.1. Initiator effect.** The effect of initiator dosage on the copolymerization was evaluated based on the grafting ratio and charge density of the lignin copolymer, and the results are

shown in Figure 7. Both the grafting ratio and charge density of LCP increased gradually with the increase in the initiator dosage up to 1.5 wt.%, which is attributed to the formation of more radicals at a higher dosage.<sup>59,60</sup> The maximum grafting ratio (39.6 %) and charge density (1.38 meq/g) were obtained at 1.5 wt.% initiator dosage. When the initiator dosage was more than 1.5 wt.%, the grafting ratio and charge density decreased. This decrease is attributed to the higher chance of collision occurring between monomer molecules to produce PAA or radical coupling termination. Figure 7 also shows the ratio of PAA produced to AA used in this copolymerization. The ratio of PAA produced to AA used during the reaction increased with an increase in the dosage of initiator used. Using an initiator dosage of 3%, 46.7 % of AA monomers were converted to PAA. Similar results were also found in the copolymerization of alkali lignin with acrylamide investigated by Fang et al.<sup>61</sup> and Lee et al.<sup>62</sup>



**Fig. 7.** Charge density and grafting ratio as a function of initiator dosage (KL 0.2 mol/L, mole ratio of AA/KL 6.0, 60 °C, 2 h)

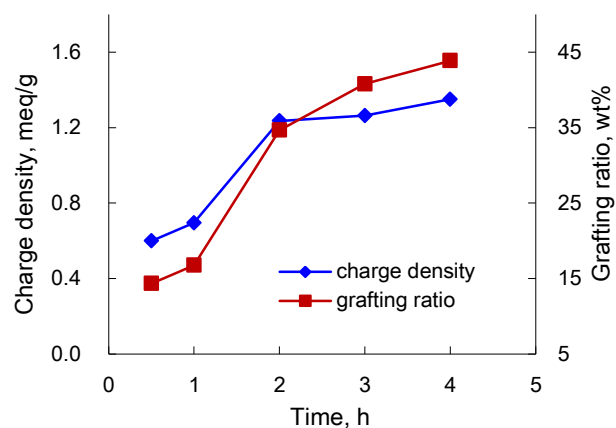


**Fig. 8.** Charge density and grafting ratio as a function of molar ratio of AA to lignin. (KL 0.2 mol/L, initiator 1.5 %, 60 °C, 2 h)

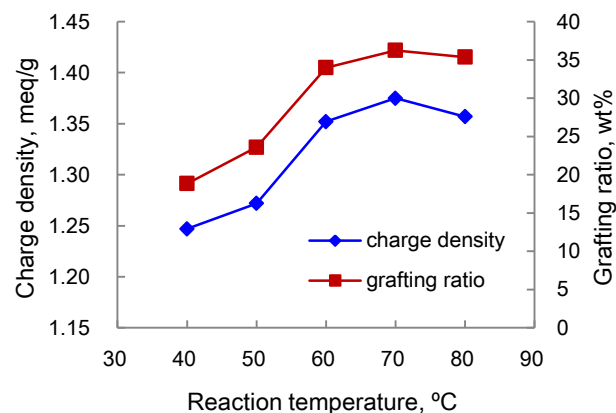
**3.2.2. AA/KL effect.** Figure 8 shows the charge density and grafting ratio of LCP as a function of mole ratio of AA to KL. The charge density was consistent with grafting ratio as both gradually increased with the increase in mole ratio of AA/KL. At a ratio of 10, the charge density and grafting ratio reached their highest values. When the ratio was increased from 10 to 13.5, the charge density and grafting ratio decreased from 1.30 meq/g to 0.80 meq/g and from 38.5 % to 33.2 %, respectively. The increases in the charge density and grafting ratio are attributed to the higher chance of collision occurring between AA and KL at higher AA to KL ratios.<sup>63</sup> However, when the ratio of AA/KL was higher than 10, the formation of PAA was

dominated, which can be confirmed by the ratio of PAA produced to AA used in the reaction shown in Figure 8. When the ratio of AA/KL was increased to 13.5, 58.3 % of AA monomers were converted into PAA, which is about 10% higher than that at the ratio of 10.

**3.2.3 Time effect.** The effects of reaction time on the charge density and grafting ratio were investigated and the results are shown in Figure 9. Both grafting ratio and charge density increased with reaction time. The grafting ratio and charge density of LCP significantly increased when the reaction time was extended from 0.5 h to 2 h. Further extension of reaction time led to a gradual increase in the charge density and grafting ratio. The increase in the charge density and grafting ratio is attributed to chain extension of LCP and the availability of hydroxyl radicals and monomer molecules.<sup>42, 64</sup>



**Fig. 9.** Charge density and grafting ratio as a function of reaction time. (KL 0.2 mol/L, initiator 1.5 %, mole ratio of AA/KL 6.0, 60 °C)



**Fig. 10.** Charge density and solubility as a function of temperature (KL 0.2 mol/L, mole ratio of AA/KL 6.0, initiator 1.5 %, 2 h)

**3.2.4. Temperature effect.** The grafting ratio and charge density of LCP are presented as a function of reaction temperature shown in Figure 10. The charge density and grafting ratio increased to 1.35 meq/g and 36 %, respectively, when the reaction temperature was to 70 °C.

To understand the main principle behind these results, the hydrodynamic diameter (hy) of KL in solution at different temperatures was investigated and the results are presented in Figure 11. The average hydrodynamic diameter and polydispersity of KL decreased from 11.2 nm and 0.377 at 40 °C to 3.1 nm and 0.299 at 80 °C, respectively. This decrease



implies that KL segments dissociate from its aggregates at a higher temperature (steric hindrance is reduced at a higher temperature), which allow the AA monomers to access the reaction sites on KL more effectively, as seen in Figure 10. This phenomenon was also reported for softwood lignin and lignosulfonate macromolecules as they tend to dissociate from its self-assembled state to an individual lignin molecule and the individual lignin molecule tend to extend their conformation at higher temperatures.<sup>44,65</sup> In addition, the results in Figure 10 may suggest that the copolymerization of KL is an endothermic reaction as it was promoted at a higher temperature.

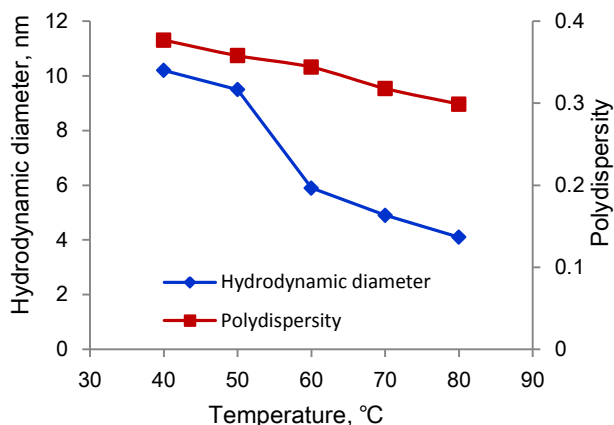


Fig.11. Hydrodynamic diameter and polydispersity of kraft lignin as a function of temperature in pH 11.0 in aqueous solution

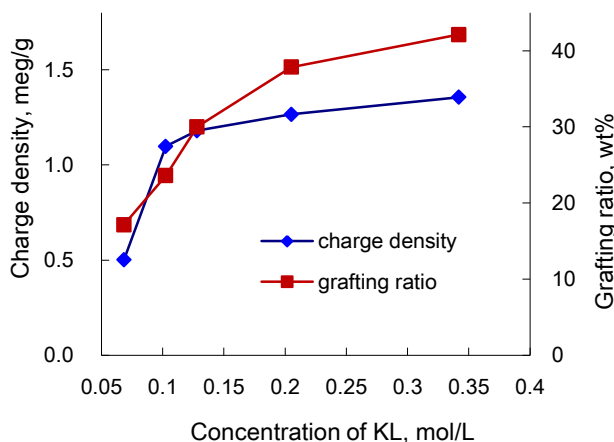


Fig.12. Charge density and grafting ratio as a function of KL concentration. (mole ratio of AA/KL 6.0, initiator 1.5 %, 2 h, 60 °C)

In Figure 10, it was also observed that when the temperature was higher than 70 °C, the charge density and grafting ratio decreased slightly, which is associated with the shorter half-life of initiator. This favours chain termination and chain transfer reactions as well as the competing PAA reaction.<sup>32,41,63</sup>

**3.2.5. Concentration effect.** The grafting ratio and charge density of LCP polymers as a function of concentration are presented in Figure 12. The charge density of LCP increased from 0.52 meq/g to 1.25 meq/g when the concentration of KL increased from 0.05 mol/L to 0.35 mol/L. The grafting ratio also increased from 17.1 % to 42.1 %. These increases are attributed to the increased probability of collision among lignin radicals, monomer radicals and the initiator molecules to form LCP.<sup>66-68</sup> Based on the results described in previous sections, the optimal

conditions for LCP production were 0.35 mol/L KL, AA/KL ratio of 8.0 mol/mol, 1.5 % initiator (based on lignin mass), 70 °C and 3 h. The properties of LCP that was prepared under these optimal conditions and KL are listed in Table 1. The same samples are used for FTIR and NMR analyses, and the lignin-acrylic acid copolymer has a charge density of 1.86 meq/g, which is significantly larger than that of KL. The MW of LCP was also increased from 17,890 g/mol (for KL) to 46,420 g/mol (for LCP).

Table 1. The properties of LCP and KL

Sample	KL	LCP
Grafting ratio, %	-	45.3
Negative charge density, meq/g	0.01	1.86
$M_n$ , g/mol	5,150	21,360
$M_w$ , g/mol	17,890	46,420
$M_w/M_n$	3.473	2.173

### 3.3. LCP characterization

**3.3.1. FTIR spectra of KL, LCP and PAA.** The LCP that had a charge density of 1.86 meq/g and grafting ratio of 45.3 % was selected for further analysis. The FTIR spectra of LCP and PAA (H-PAA) are presented in Figure 6, while that of KL is presented in Figure 5. In the FTIR spectra, two absorption bands centring at 1266  $\text{cm}^{-1}$  and 1140  $\text{cm}^{-1}$  are assigned to the C-O and C-H stretch of guaiacyl unit, respectively, being representative of softwood kraft lignin.<sup>69</sup> The broad peak at 3425  $\text{cm}^{-1}$  is assigned to the hydroxyl groups. The characteristic bands for the aromatic skeletal vibration of KL were located at around 1591, 1510 and 1423  $\text{cm}^{-1}$ , respectively.<sup>69</sup>

The spectrum of LCP had strong absorption peaks at 1558  $\text{cm}^{-1}$  and 1406  $\text{cm}^{-1}$ , which were absent in spectrum of KL. These two peaks belong to carboxylic acids (symmetrical stretching vibrations of carboxyl anions  $-\text{COO}^-$ ), as were also observed in spectrum of PAA, illustrating the successful copolymerization of lignin with AA.<sup>70</sup> The absorption peak at 1510  $\text{cm}^{-1}$  in the spectrum of LCP demonstrated the existence of aromatic ring of lignin.<sup>32</sup> More interestingly, the results in Figure 5 and Figure 6 also show that the relative intensity of the band at 1028  $\text{cm}^{-1}$ , which belongs to non-etherified Ph-OH groups<sup>52</sup>, is weaker in LCP than in KL, suggesting that lignin participated in the copolymerization reaction through its active phenolic group.

**3.3.2.  $^1\text{H-NMR}$  analysis.** The NMR spectra of KL and LCP are shown in Figure 13(a) and 13(b) respectively, while the spectrum of PAA (H-PAA) is shown in Figure 4. In Fig. 13(a), the peak at 9.4 ppm is attributed aldehyde proton; at 8.47 ppm is attributed to unsubstituted phenolic protons; at 7.42 ppm is associated with substituted phenolic protons; at 6.93-6.15 ppm is attributed to aromatic protons including certain vinyl protons on the carbons adjacent to aromatic rings; at 5.75-5.15 ppm is attributed to aliphatic protons including  $\text{H}_\alpha$  and  $\text{H}_\beta$ ; at 3.25-3.81 ppm is attributed to protons in methoxyl groups of lignin; and at 3.36 ppm is assigned to the methylene protons in  $\beta$ - $\beta$  structure.<sup>71</sup> In the spectrum of PAA (H-PAA) in Figure 4, peaks appeared at 1.6 ppm is attributed to C-1, at 2.2 ppm is attributed to C-2, and 2.6 ppm is assigned to hydroxyl end groups of PAA.<sup>41</sup> In Figure 13(b), it is observed that the peaks for PAA chain segment appeared at 1.6 ppm, 2.2 ppm and 2.6 ppm, respectively, and also the peaks for lignin presented at 3.36 ppm, 3.81 ppm, 6.65 ppm, 7.42 ppm, 8.47 ppm and 9.4 ppm, which illustrates the successful copolymerization of lignin and AA. In addition, a peak at 4.30 ppm is presented in the spectrum of LCP, which is not observed in that of KL and is attributed to

the protons of CH<sub>2</sub> in the structure of -CH<sub>2</sub>COC<sub>6</sub>H<sub>5</sub>.<sup>72</sup> This also confirms that the phenolic group was an active site participated in the copolymerization reaction, which is consistent with the FTIR results discussed in Figure 6.<sup>73-75</sup>

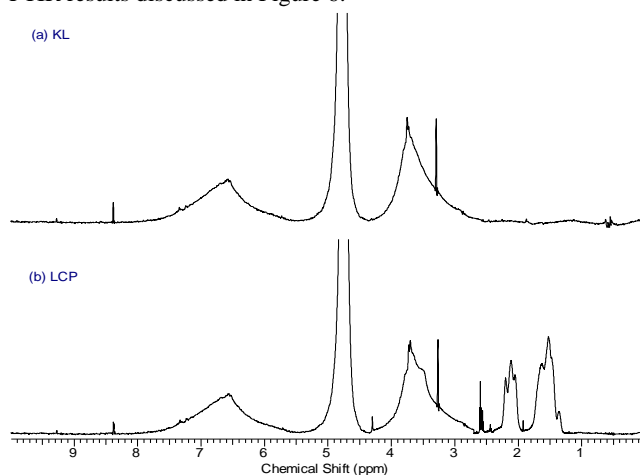


Fig. 13. <sup>1</sup>H-NMR spectra of KL and LCP

**3.3.3. Solubility analysis.** The solubility of LCP and KL were presented as a function of pH in Figure 14. At pH 10, the solubility of KL dropped dramatically to less than 20 g/L. Interestingly, LCP was soluble under acidic condition to pH 4. Below this pH, the solubility of LCP dropped considerably. As is well known, the pK<sub>a</sub> of carboxylic acid is around 4.35, which justifies that the solubility of LCP is due to the carboxyl groups at a pH that is higher than 4.0.<sup>76</sup> It is observed that at pH 7, KL has a very low solubility (1.8 g/L), however, LCP has 100 g/L solubility, which illustrated that the dramatic increase in the solubility of KL via this copolymerization.

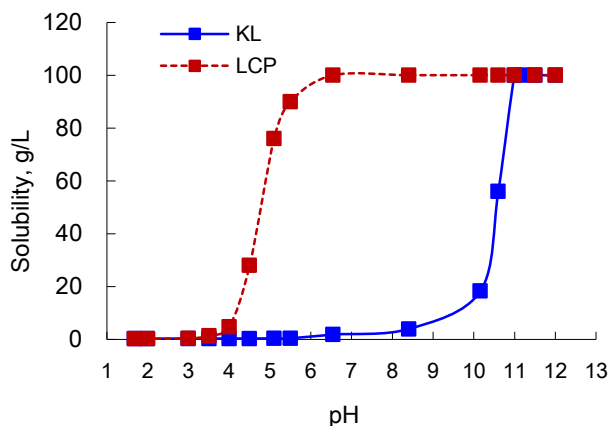


Fig.14. Solubility of LCP and KL as a function of pH

## 4. Conclusions

In this work, a water soluble kraft lignin copolymer (LCP) was successfully prepared by the copolymerization of softwood KL and acrylic acid using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> as an initiator under alkaline condition. The charge density analysis and grafting ratio were used to evaluate the influences of reaction conditions on the copolymerization. We found that the existence of phenolic groups on KL favoured the formation of LCP and the optimal conditions for the copolymerization were 0.35 mol/L KL, AA/KL ratio of 8.0 mol/mol, 1.5 wt.% initiator, 70 °C and 3 h. NMR and FTIR analyses confirmed the successful

copolymerization of KL with AA. Additionally, the resulting LCP is water soluble at neutral pH.

Under the optimized conditions, the charge density and molecular weight of LCP were 1.86 meq/g and 46,420 g/mol, respectively. The results also confirmed that LCP was soluble under acidic conditions to pH 4. This LCP can potentially be used as a dispersant for cement admixture or flotation ore or as a flocculant for tailing wastes in the mining industry.

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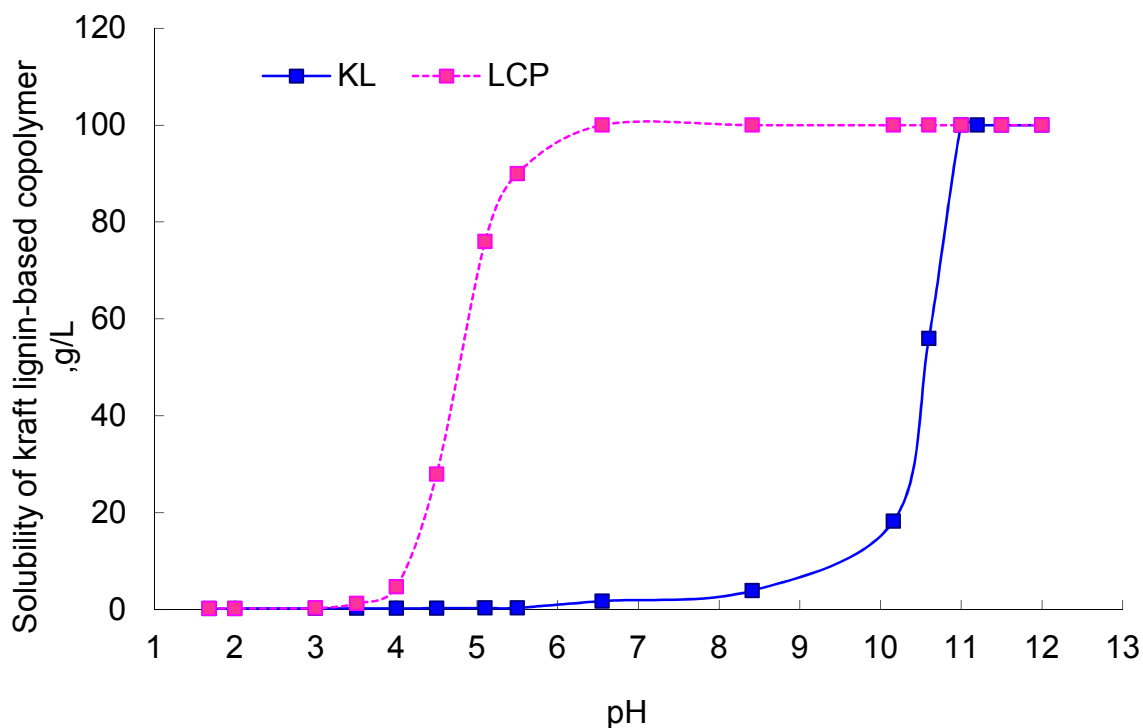
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## Water soluble kraft lignin-acrylic acid copolymer: synthesis and characterization

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In this work, softwood kraft lignin was copolymerized with acrylic acid, which generated a water soluble product at pH 7.