

Preparation of an Amphoteric Lignin Copolymer and Its Value in the Papermaking Industry

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Lignin biomass is an important renewable woody material that can be converted into high value-added products through physical and chemical reactions, such as paper strength additives. In this study, a cationic methacryloyloxyethyl trimethylammonium chloride monomer (DMC) and anionic acrylic monomer (AA) were grafted onto softwood kraft lignin through free radical polymerization to prepare an amphoteric lignin copolymer. Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance spectroscopy (¹H NMR), elemental analysis, and charge density analysis methods confirmed that the anionic and cationic monomers were successfully grafted onto the lignin. The grafting ratios of AA and DMC monomer in the lignin-DMC-AA copolymer were 62.4% and 51.3%, respectively. The application of lignin-DMC-AA copolymer as a paper additive for enhancing the physical properties of paper sheets was studied in the papermaking industry. The results indicated that the copolymer had a maximum increase in physical strength at around 2 wt% lignin-DMC-AA. The amount absorbed on the fibers was 18.5 mg/g, and the retention of the lignin-DMC-AA copolymer was over 90%.

Keywords: Softwood kraft lignin; Amphoteric lignin copolymer; Paper additive; Physical properties

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INTRODUCTION

Lignin is a heterogeneous and amorphous polymer that constitutes a large part of the cell wall, making it the second largest biomass after cellulose (Saito *et al.* 2012; Marino *et al.* 2016). Lignin accounts for 15 to 35% of the cell walls in terrestrial plants, which is generally considered a waste for low-value applications (Kai *et al.* 2016; Banu *et al.* 2019). Some chemical modifications can alter the properties of lignin and make it have high value utilization to fully realize its potential (Fang *et al.* 2010; Gao *et al.* 2019; Hajirahimkhan *et al.* 2019). These chemical modifications give lignin better miscibility over other polymeric matrices, thus improving the performance of lignin-based composites (Wang *et al.* 2011; Thakur *et al.* 2014; Liu *et al.* 2015).

Low-cost lignin has high carbon content, high thermal stability, biodegradability (Triwulandari *et al.* 2019), antioxidant activity, and favorable stiffness (Ten and Vermerris 2015; Thakur and Thakur 2015; Li *et al.* 2019b). These attributes have attracted a large number of researchers. Lignin-based resin was prepared with kraft lignin and glycerol to replace formaldehyde-based adhesives (Li *et al.* 2018). Meister *et al.* (2010) successfully

prepared the lignin graft copolymer, which had a good effect as a mud thinner for drilling operations. Cai *et al.* (2017) successfully synthesized amphoteric lignin surfactant (SLQA) through the quaternization of sulfonated lignin, which could enhance the enzymatic hydrolysis of lignocellulose. Wang *et al.* (2016) developed a soda lignin-acrylamide copolymer, which can significantly enhance the physical properties of paper. Previously, the effects of three different lignin polymers as a paper dry-strength additive on pulp properties were studied (Liu *et al.* 2018). However, the amount absorbed on the fibers and the retention of lignin copolymer have not yet been studied. Moreover, it is rare to use lignin-based materials as paper additives in the paper industry according to current research (Wang *et al.* 2016).

In this study, amphoteric lignin copolymer was prepared by free radical polymerization using softwood kraft lignin as raw material, which can be used to improve the paper's physical properties as a strengthening agent. The main objectives were as follows: (1) production of an amphoteric lignin copolymer and analysis characterization through various analytical techniques; (2) Analysis of amphoteric lignin copolymer as a strengthening agent to improve the paper's physical properties. Additionally, the physical properties of the paper sheets were determined to measure the tensile, tear, and burst indices. The absorption of the amphoteric lignin copolymer on the pulp fibers was measured by a polyelectrolyte titration method after retention experiments for doses of 0.5 to 3% amphoteric lignin copolymer relative to pulp.

EXPERIMENTAL

Materials

Kraft pulping black liquor was used to produce softwood kraft lignin by an acid precipitation process (Kim 2015). Methacryloxyethyltrimethyl ammonium chloride (DMC) and acrylic acid (AA) were used as the grafting monomer as received from Sigma-Aldrich (Beijing, China). Potassium persulfate (KPS) as an initiator reagent was purchased from Sigma-Aldrich and used without further purification. Anionic polyvinyl sulfate (PVSK) and cationic polydiallyldimethylammonium chloride (PDADMAC) (Macklin, Shanghai, China) standard samples were diluted in ultrapure water. The alkaline peroxide mechanical pulp (APMP) was obtained from Shandong Sun Paper Industry (Jining, China).

Preparation of Amphoteric Lignin Copolymer

The preparation of amphoteric lignin copolymer was completed using DMC and AA as monomers, according to the earlier method by Liu *et al.* (2018). Here, 1 g of lignin was dispersed in 40 mL of ultrapure water and stirred at 400 rpm. Then, NaOH solution (0.1 M) was used to adjust the pH of lignin solution to 11. The lignin solution was heated to 75 °C for 30 min, and then the pH was adjusted to 4 using sulfuric acid (0.1 M). Nitrogen was used for 30 min to remove oxygen from the solution, and a certain amount of KPS was added as an initiator. After 10 min, the DMC monomer was added dropwise to the solution, and then the AA monomer was added to the solution. The copolymerization reaction of lignin with anionic and cationic monomers was carried out at 75 °C for 3 h. Next, the lignin solution was cooled, and ethanol/water (80 vol%) was added to precipitate the amphoteric lignin copolymer. The precipitate was washed twice with ethanol/water (80 vol%) and dried at 105 °C to produce a purified amphoteric lignin copolymer (lignin-DMC-AA copolymer).

Analytical Methods

FTIR analysis

The lignin and lignin-DMC-AA copolymer samples were investigated using a Fourier transform infrared spectrophotometer (FTIR, Bruker VERTEX70; Bruker, Karlsruhe, Germany). Here, a 5 mg sample of lignin and lignin-DMC-AA copolymer was used and recorded with 32 scans in transmittance mode.

¹H NMR analysis

The proton nuclear magnetic resonance (¹H-NMR) spectroscopy analysis of lignin and lignin-DMC-AA copolymer samples used a nuclear magnetic resonance (NMR) spectrometer (Bruker AVANCE II 400 MHz; Bruker, Karlsruhe, Germany). Approximately 10 mg of the lignin and lignin-DMC-AA copolymer sample were dissolved in D₂O and recorded over 32 scans.

Thermal analysis

The thermal analysis of lignin and lignin-DMC-AA copolymer samples was performed using a thermogravimetric analyzer (TGA Q50; TA, New Castle, DE, USA). Samples of 3 to 10 mg lignin and lignin-DMC-AA copolymer were studied using nitrogen as protective gas from 50 to 600 °C at 10 °C/min.

Elemental analysis

Elemental analysis of lignin and lignin-DMC-AA copolymer samples were measured using an elemental analyzer (Vario EL III; Elementar, Hanau, Germany). Two to five samples of lignin and lignin-DMC-AA copolymer samples were used while the detection temperature was raised to 1150 °C.

Charge density analysis

Approximately 20 mg of lignin and lignin-DMC-AA copolymer samples were dissolved in a certain amount of ultra-pure water, and ultrasonicated at 30 °C for 1 h. A particle charge detector (PCD 04; Mutek, Berlin, Germany) was performed to measure the charge density of the lignin solution with 0.001 M PDADMAC and PVSK standard solutions.

Molecular weight analysis

Approximately 5 mg of lignin and lignin-DMC-AA copolymer samples were dissolved in NaNO₃ solution (0.1 M) at 35 °C and continuously stirred at 500 rpm for 36 h. Then, 0.2-μm nylon filters were used to filter the sample solutions, which was used to determine the lignin molecular weight by gel permeation chromatography (LC-20AD; Shimadzu, Tokyo, Japan). The chromatographic columns of PolyAnalytic PAA 203 and PAA 206 were used at 35 °C, while NaNO₃ solution (0.1 M) was considered as the sample solvent and eluent. The flow rate of the sample solution was set to 0.50 mL/min.

Grafting ratio

The grafting ratio of lignin-DMC-AA copolymer sample was identified using Eq. 1 according to the previous calculation method (Wang *et al.* 2015),

$$\text{Grafting ratio} = (N / 14 \times M_w(\text{DMC})) / (100 - N / 14 \times M_w(\text{DMC})) \times 100 \quad (1)$$

where N is the nitrogen content of samples (wt%), and M_w (DMC) is the molecular weight of DMC (207.7 g/mol).

The carboxylate group content of lignin-DMC-AA copolymer sample was measured using an automatic potentiometer (905 Titrado; Metrohm, Berne, Switzerland). A sample of 1 g of lignin and lignin-DMC-AA copolymer was dissolved in 100 mL of ultrapure water and ultrasonicated for 30 min, and then the pH value of the sample solution was adjusted to 10.5. Finally, the sample solution was titrated dropwise with the cationic surfactant to measure the carboxylate content of the sample. The grafting ratio was calculated using Eq. 2 (Bayazeed *et al.* 1989),

$$\text{Grafting ratio} = (C \times M_w(\text{AA})) / (1 - C \times M_w(\text{AA})) \times 100 \quad (2)$$

where C is the total carboxylate group content (mmol/g), and M_w (AA) is the molecular weight of AA (72 g/mol).

Performance Assessments of Amphoteric Lignin Copolymer as Strengthening Agent

The performance of lignin-DMC-AA copolymers as a strengthening additive was evaluated using APMP (a chemi-mechanical pulp used in making most kinds of paper). In this experiment, the lignin-DMC-AA copolymer sample was first dissolved in ultrapure water by stirring the sample for 2 h at 30 °C. From 0 to 3 wt% dosage of lignin-DMC-AA copolymer were then added to the 1% pulp slurry, respectively. Before formation of the paper sheets, the pulp slurry containing lignin-DMC-AA copolymer was continuously stirred at 1500 rpm for 5 min. Formed paper sheets were dried at 97 °C for 7 min. Paper sheets were tested for tensile and tear indices with a grammage of 60 g/m²; burst index and the internal bond strength were tested with a grammage of 100 g/m². Before testing the physical strength properties of the paper, the paper sheet was held at 23 °C and 50% humidity for 24 h (Wang *et al.* 2016). After drying, the tensile, burst, and tear strengths, brightness, as well as the internal bonding strength of the handsheets, were measured according to the TAPPI T494 om-88 (1988), TAPPI T403 om-91 (1991), TAPPI T414 om-88 (1988), TAPPI T452 om-92 (1992), and TAPPI T569 om-14 (1996) standards, respectively. All data described here were the average value of three repetitions.

Absorption of Lignin-DMC-AA Copolymer on the Pulp Fibers

For the absorption measurements, 5 g of pulp was dispersed in water at high speed, and 0 to 3% lignin-DMC-AA copolymer was added for production of paper sheets. The pulp and the lignin-DMC-AA copolymer (total volume 1 L) interacted with each other for 15 min under stirring conditions and then underwent dehydration treatment. After dehydration, the filtrate was titrated with PCD for charge titration. The content of lignin-DMC-AA copolymer in the filtrate was calculated according to an appropriate standard curve. These were created according to the work on the cationic xylan copolymer (Deuschle *et al.* 2014).

Lignin-DMC-AA Copolymer Retention

The amount of nitrogen in the paper with different amounts of lignin polymer was determined *via* elemental analysis. The lignin-DMC-AA copolymer retention was calculated according to Eq. 3,

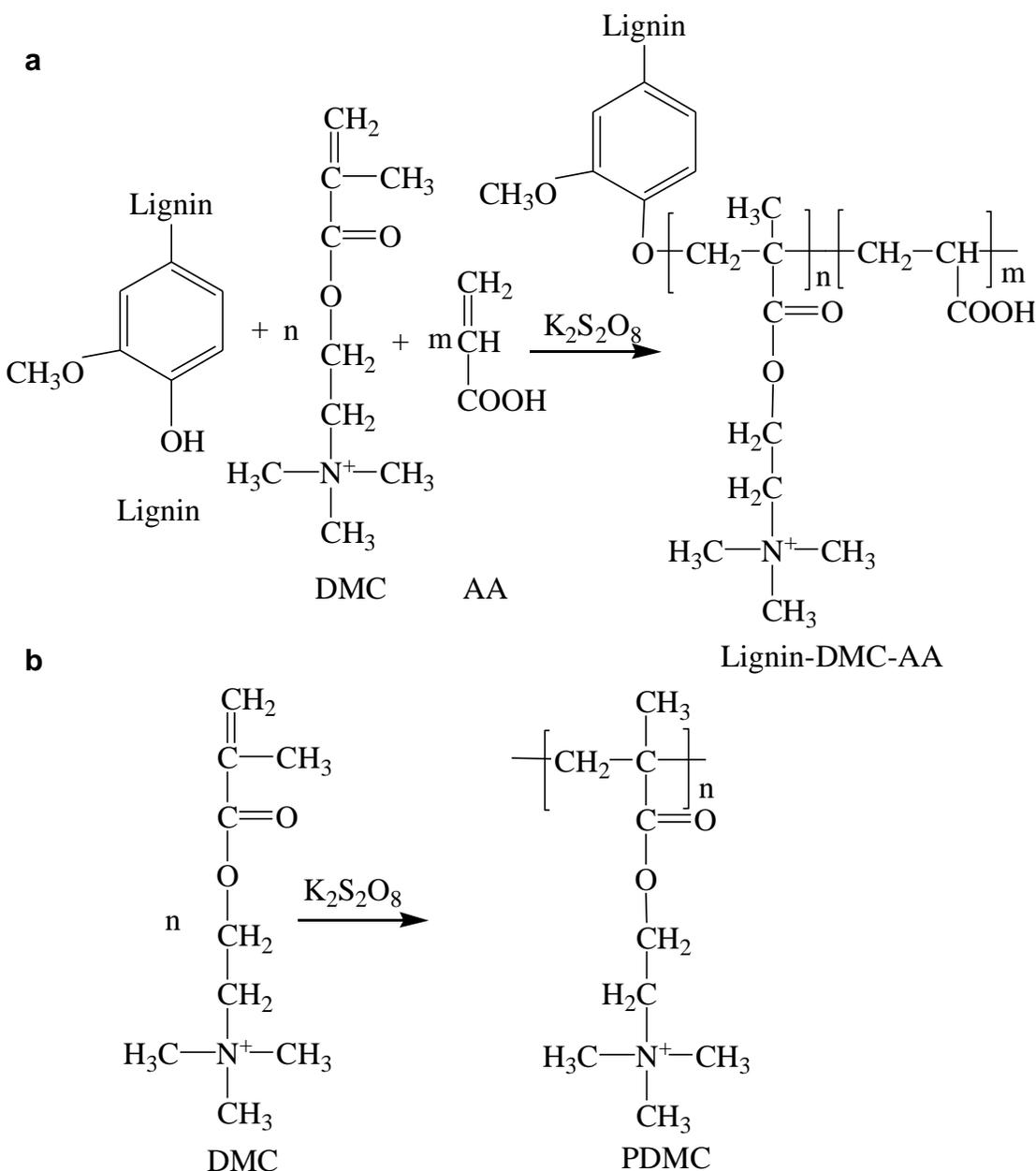
$$\text{Retention} = N \times M / (N_o \times M_o) \times 100\% \quad (3)$$

where N is the nitrogen content of paper (wt%), N_0 is the nitrogen content of lignin-DMC-AA copolymer (wt%), M is the quality of the paper (g), and M_0 is the addition of the lignin-DMC-AA copolymer (g).

RESULTS AND DISCUSSION

Preparation of the Amphoteric Lignin Copolymer

The reaction mechanisms of lignin, DMC, and AA are shown in Fig. 1. The KPS was added to the lignin solution as an initiator, resulting in lignin free radicals on the phenolic hydroxyl group. Moreover, the alkenyl groups of the DMC and AA monomers have high activity and can generate monomer-free radicals.



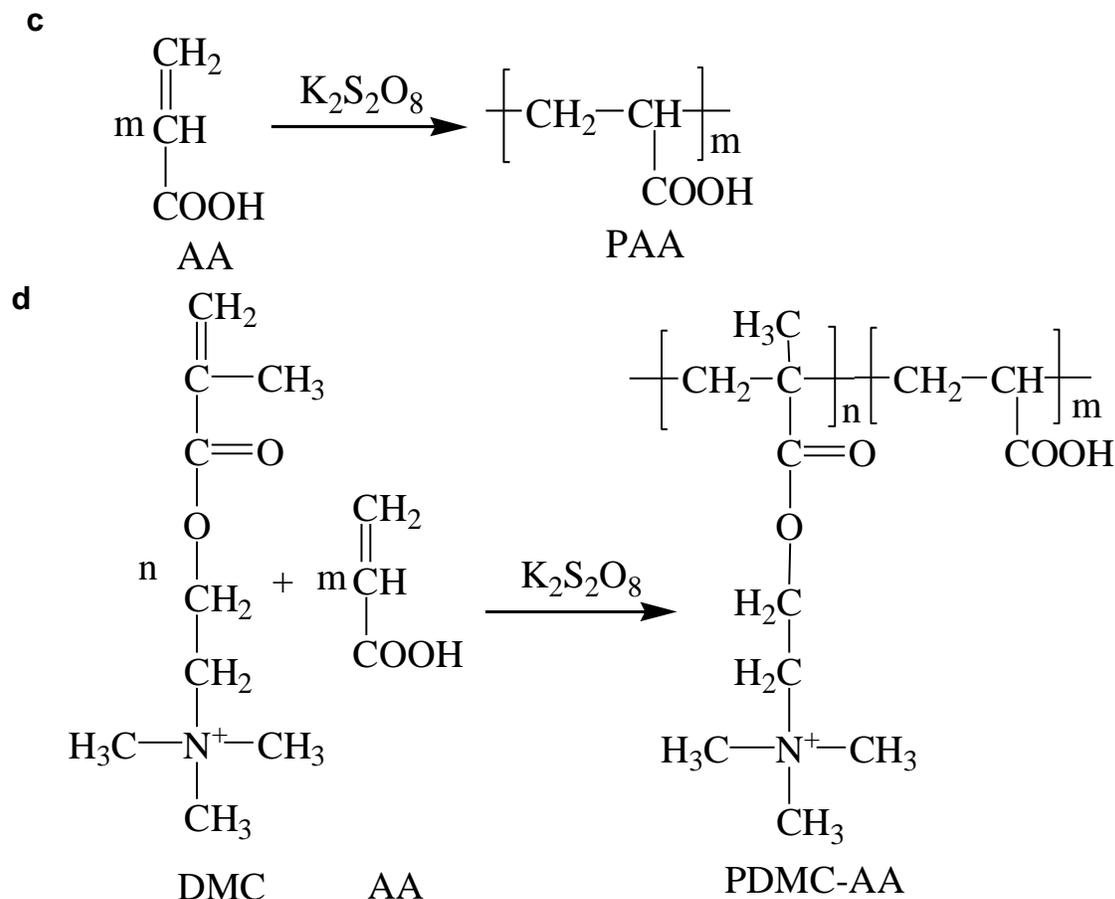


Fig. 1. Mechanism of the copolymerization of lignin with DMC and AA monomers (a: lignin-DMC-AA; b: PDMC; c: PAA; and d: PDMC-AA)

These active free radicals become receptors for lignin free radicals, leading to the chain initiation of the amphoteric lignin copolymers (lignin-DMC-AA) (Wang *et al.* 2015). Furthermore, the above reaction was accompanied by side reactions to produce homopolymers of PDMC, PAA, and PDMC-AA.

FTIR Analysis

The FTIR spectra of the lignin and amphoteric lignin copolymer are shown in Fig. 2. The strong peak at 3440 cm^{-1} was assigned to the O–H of the lignin and amphoteric lignin copolymer (Yu *et al.* 2016; Bian *et al.* 2018; Li *et al.* 2019a). The three absorption peaks at 1612 cm^{-1} , 1514 cm^{-1} , and 1456 cm^{-1} are attributed to the aromatic skeletal vibrations from lignin and amphoteric lignin copolymer (Santos *et al.* 2012; Zhang *et al.* 2017). The peak at 2938 cm^{-1} originated from the C–H stretching vibration (Konduri *et al.* 2015; Sarma *et al.* 2018). The absorption bands at 1219 cm^{-1} and 1121 cm^{-1} are assigned to the C–O and C–H stretching of the guaiacyl unit (Kong *et al.* 2015). The two peaks at 1716 cm^{-1} and 961 cm^{-1} were attributed to the C=O (DMC and AA) and quaternary ammonium group (DMC), respectively (Wang *et al.* 2015). These peaks indicated that the amphoteric lignin copolymer had been successfully prepared.

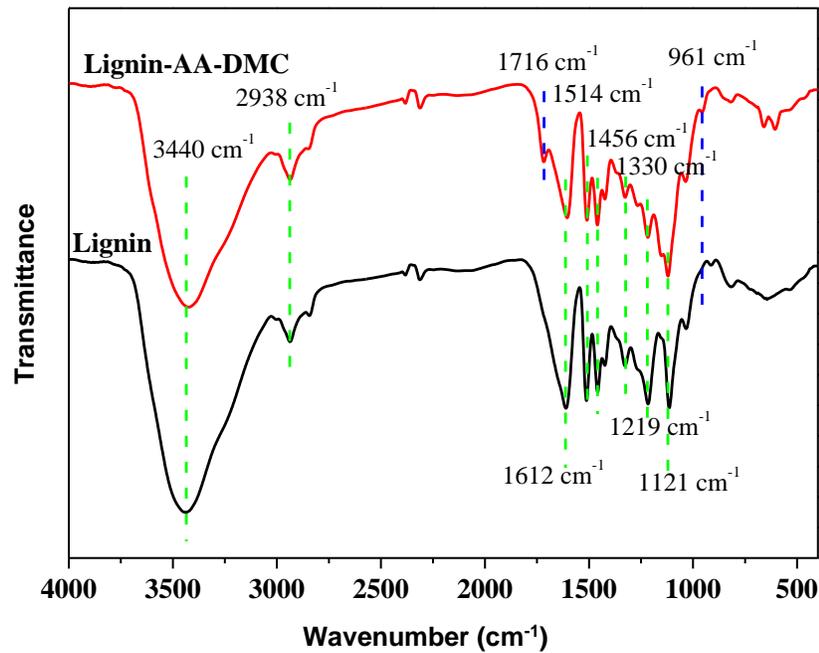


Fig. 2. FTIR spectra of lignin and amphoteric lignin copolymer (lignin-DMC-AA)

¹H NMR Analysis

The ¹H NMR spectra of the lignin and amphoteric lignin copolymer are shown in Fig. 3.

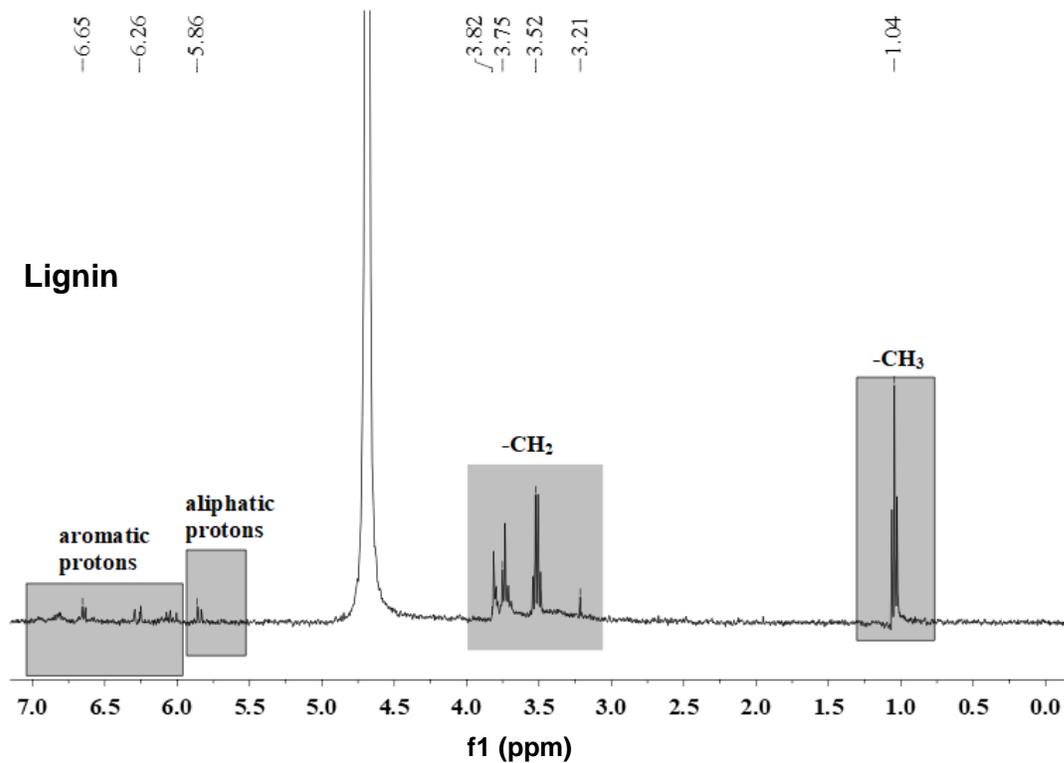


Fig. 3. A) ¹H-NMR spectra of lignin

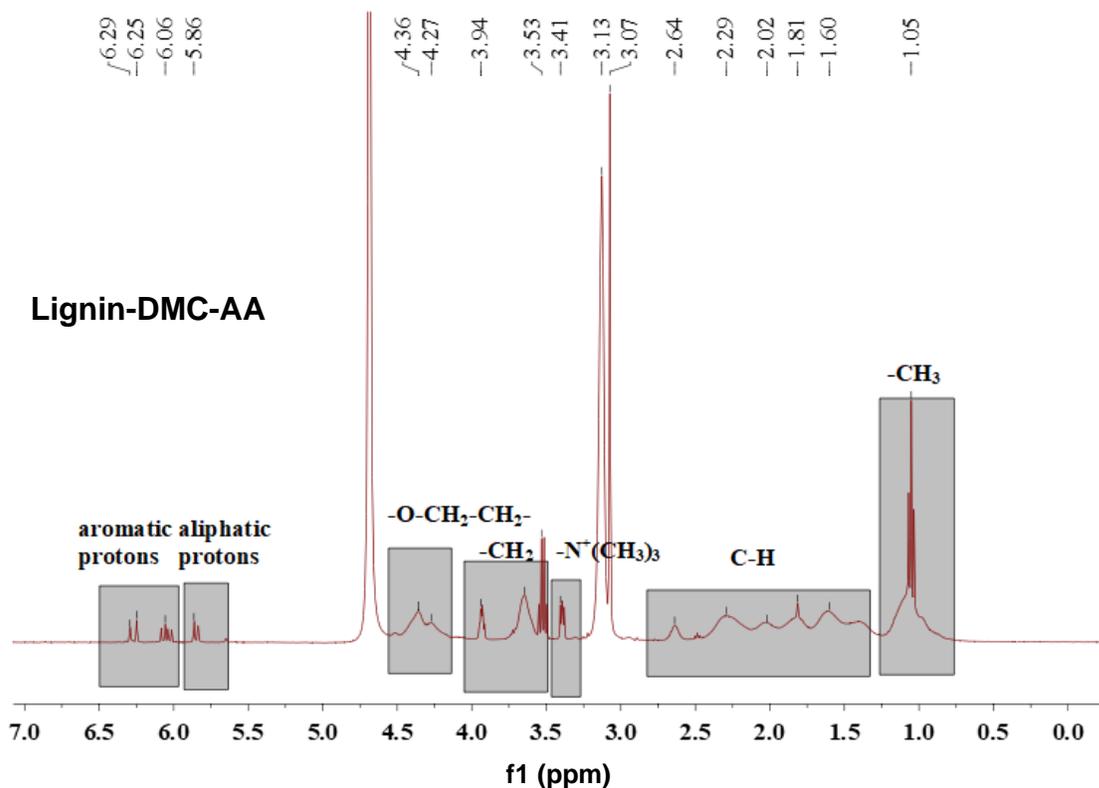


Fig. 3. B) $^1\text{H-NMR}$ spectra of amphoteric lignin copolymer (lignin-DMC-AA)

The peaks at 6.0 to 7.0 ppm are mainly due to aromatic protons, and the peaks at 5.1 to 5.9 ppm are due to aliphatic protons. The peaks at 3.0 to 4.0 ppm originate from the methoxyl groups of lignin and amphoteric lignin copolymer (Li *et al.* 2017); the peak at 3.2 ppm is attributed to the $-\text{CH}_2$ structure from lignin and amphoteric lignin copolymer. The peaks appearing from 0.9 to 1.1 ppm originate from the $-\text{CH}_3$ structure from lignin and amphoteric lignin copolymer (Nagy *et al.* 2010). The peaks at 4.5 to 5.0 ppm are attributed to the solvent of the lignin and amphoteric lignin copolymer (D_2O).

Relative to the spectrum of lignin, the characteristic signal at 3.4 ppm can be attributed to $-\text{N}^+(\text{CH}_3)_3$ protons, and the characteristic signals near 3.9 ppm and 4.3 ppm are assigned to the methylene proton ($-\text{O}-\text{CH}_2-\text{CH}_2-$) from the DMC monomer of the amphoteric lignin copolymer (Li *et al.* 2011). The peaks from 1.4 to 2.2 ppm originate from C-H, and the peak at 2.6 ppm is assigned to the hydroxyl end from the AA monomer of the amphoteric lignin copolymer (Witono *et al.* 2013). The above results indicated that the amphoteric lignin copolymer was prepared.

Thermogravimetric Analysis

The lignin and lignin-DMC-AA copolymer samples were analyzed using nitrogen as protective gas, and results are shown in Fig. 4. The weight of lignin and lignin-DMC-AA copolymer samples decreased with increased temperature from 50 to 100 $^\circ\text{C}$, which was due to the loss of moisture (Ünlü *et al.* 2015). The thermal characteristics of lignin and lignin-DMC-AA copolymer were analyzed. The main degradation temperature of lignin weight ranged from 250 to 500 $^\circ\text{C}$. The temperature range of amphoteric lignin copolymer

samples was 200 to 500 °C. The maximum degradation rate of lignin and amphoteric lignin copolymer was slightly different, which is represented by T_{max} (maximum weight loss) at 385 and 397 °C, respectively. The lignin remained approximately 40 wt%; lignin-DMC-AA copolymer remained approximately 30 wt%. The above analysis showed that some chemical modifications lead to a certain degree of reduction in the thermal stability of the final product, which was contributed to the degradation of the new access group described in previous studies (Kong *et al.* 2015; Baniasad and Ghorbani 2016; Liu *et al.* 2018).

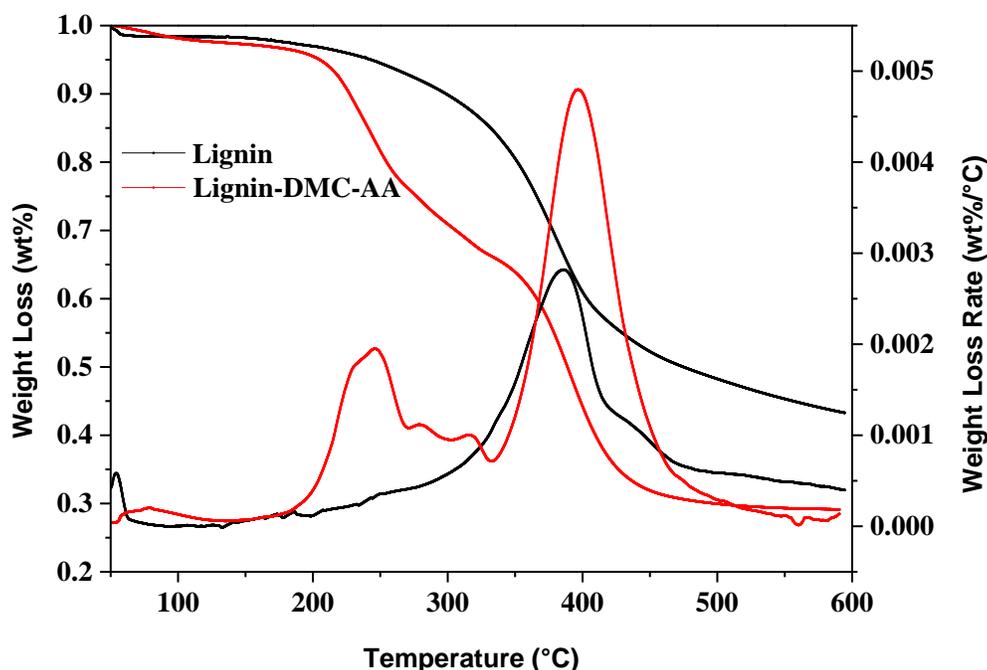


Fig. 4. Weight loss and weight loss rate of lignin and lignin-DMC-AA copolymer

Properties of Lignin and Lignin-DMC-AA Copolymer

The properties of the lignin and lignin-DMC-AA copolymer are shown in Table 1.

Table 1. Properties of Lignin and Lignin-DMC-AA Copolymer

Samples	Lignin	Lignin-DMC-AA
C (wt%)	63.51	55.34
H (wt%)	6.21	6.08
O (wt%)	30.57	26.32
N (wt%)	0.004	2.591
Molecular formula	$C_9H_{10.56}O_{3.25}$	$C_9H_{11.86}O_{3.21}N_{0.36}$
DMC (Graft ratio (%))	--	62.44
AA (Graft ratio (%))	--	51.28
Charge density (mmol/g)	-0.002	+0.946
M_n (g/mol)	1.725×10^4	3.647×10^5
M_w (g/mol)	2.600×10^4	4.256×10^5
M_w/M_n	1.51	1.17

The charge densities of the lignin and lignin-DMC-AA copolymer dramatically increased from -0.002 mmol/g to $+0.946$ mmol/g. The grafting ratios of AA and DMC in the lignin-DMC-AA copolymer were 62.4% and 51.3%, respectively. Compared with unmodified lignin, lignin-DMC-AA copolymer had slightly higher weight average molecular weight (M_w) and number average molecular weight (M_n). The polydispersity (M_w/M_n) of lignin and lignin-DMC-AA copolymer showed the change of molecular weight distribution. In addition, the N content of the lignin-DMC-AA copolymer remarkably increased from 0.004 to 2.591wt% due to the amide group grafted onto the lignin. Therefore, the above analysis indicated that the copolymerization of DMC and AA monomer and lignin successfully changed the elemental content and charge density of lignin.

Application of Lignin-DMC-AA Copolymer as a Strengthening Agent in Papermaking

The results in Fig. 5 indicate that the lignin-DMC-AA copolymer can act as strength additive to improve the physical properties of paper sheets. As the dosage of lignin-DMC-AA copolymer was increased, the tear, tensile, and burst indices increased remarkably. The increase in the paper strength was attributed to the formation of H bonding between the lignin-DMC-AA copolymer and cellulose fibers (Wang *et al.* 2016). At 2 wt% dosage of the lignin-DMC-AA copolymer, the maximum increases of 48.8%, 71.4%, and 65.1%, were obtained for burst, tensile, and tear indices, respectively. However, when the dosage of lignin-DMC-AA copolymer was further increased, the strength of the paper sheet decreased slightly. This decrease was due to an excess of lignin-DMC-AA copolymer, which lowered the retention of the lignin-DMC-AA copolymer on the fibers. This was due to the total amount of fiber remaining constant, while the positive and negative ions of lignin-DMC-AA copolymer were fixed to the surface of the fiber by adsorption, which was limited by the specific surface area of the fiber (Kong *et al.* 2018).

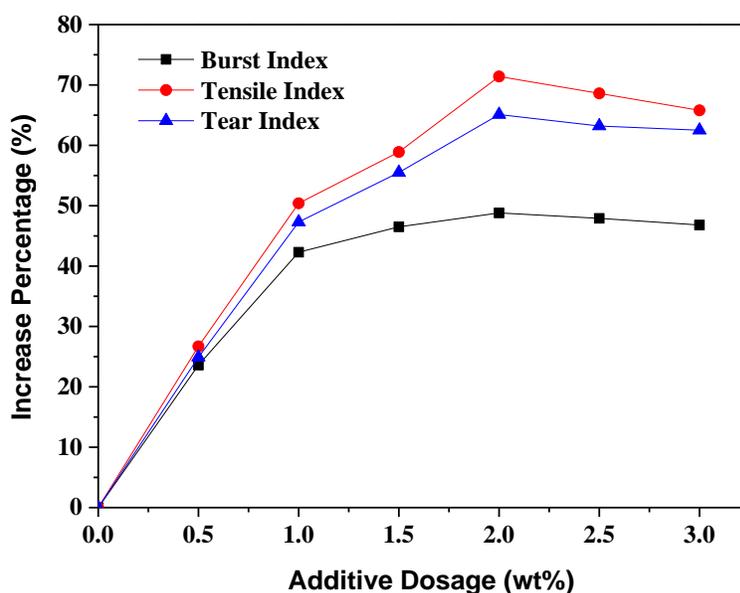


Fig. 5. Paper properties as function of lignin-DMC-AA copolymer dose

The increase in the physical strength of paper sheets was attributed to the formation of an ionic bond between the amide groups of lignin-DMC-AA copolymer and negative charge of pulp fibers. It was also reported that the hydrogen bonding can be formed between the OH groups of starch and carboxyl (COOH) groups of carboxymethyl cellulose (Tavares *et al.* 2020). Here, it would also be some hydrogen bonding development between the COO⁻ groups of lignin-DMC-AA copolymer and OH groups of pulp fibers, which prompted the increase of internal bonding strength (see Table 2) and connections between fibers. The bonding development of lignin-DMC-AA copolymer and pulp fibers prompted the adsorption of lignin-DMC-AA copolymer on fibers. The lignin-DMC-AA copolymers were adsorbed between adjacent fibers (Fig. 6), such that the DMC and AA segments of the lignin-DMC-AA copolymer would bridge each other and remarkably enhance the bonding between the fibers (Wang *et al.* 2016).

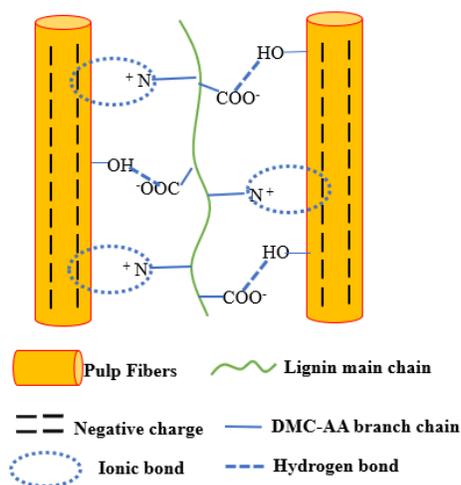


Fig. 6. Bridging of fibers by lignin-DMC-AA copolymer

Table 2 shows the changes in the internal bond strength and brightness of paper sheets using 2 wt% lignin and lignin-DMC-AA copolymer as a paper strengthening agent. The results indicated that the internal binding strengths of lignin-DMC-AA product increased by 64.9%, compared with that of no additives and only using lignin as additives, which was due to the H bonds and ionic bonds generating between the lignin-DMC-AA copolymer and cellulose fibers. The brightness of paper without additives is 76 % ISO, and the brightness of paper at additive dosages 2.0% drops slightly by 1 % ISO, which would give a smaller decrease in the brightness of corrugated paper and cardboard paper.

Table 2. Internal Bond Strength and Brightness of the Paper

Samples	No additives	Lignin	Lignin-DMC-AA copolymer
Internal bonding strength (J/m ²)	180	185	305
Brightness (% ISO)	76.0	75.6	75.0

Absorption of Lignin-DMC-AA Copolymer on the Pulp Fibers

The amount of absorbed lignin-DMC-AA copolymer on the pulp fibers was calculated (mg/g; Fig. 7). Relative to the amount of additives, the absorption behavior of

the fiber and the strength characteristics of the paper (Fig. 5) demonstrated the same increasing trend when the dosage of lignin-DMC-AA copolymer increased. With increasing amount of absorbed lignin-DMC-AA copolymer on the pulp fibers, the amount absorbed on the fibers reached a maximum of 18.5 mg/g at 2 wt% dosage, while the increase in paper strength plateaued. This was because the total amount of fiber remained constant, while the positive and negative ions of lignin-DMC-AA copolymer were fixed to the surface of the fiber by adsorption, which was limited by the specific surface area of the fiber (Kong *et al.* 2018).

When the addition amount of lignin exceeds 2%, the increase in the cationic charge repulsion between the lignin polymers will result in a decrease in the amount of adsorption on the fiber. The ionic bond between the amide groups, negative charge of cellulose fibers, the hydrogen bonding development of lignin-DMC-AA copolymer, and negative charge of fibers balanced the electrostatic repulsion between the fiber and carboxyl group of lignin-DMC-AA copolymer.

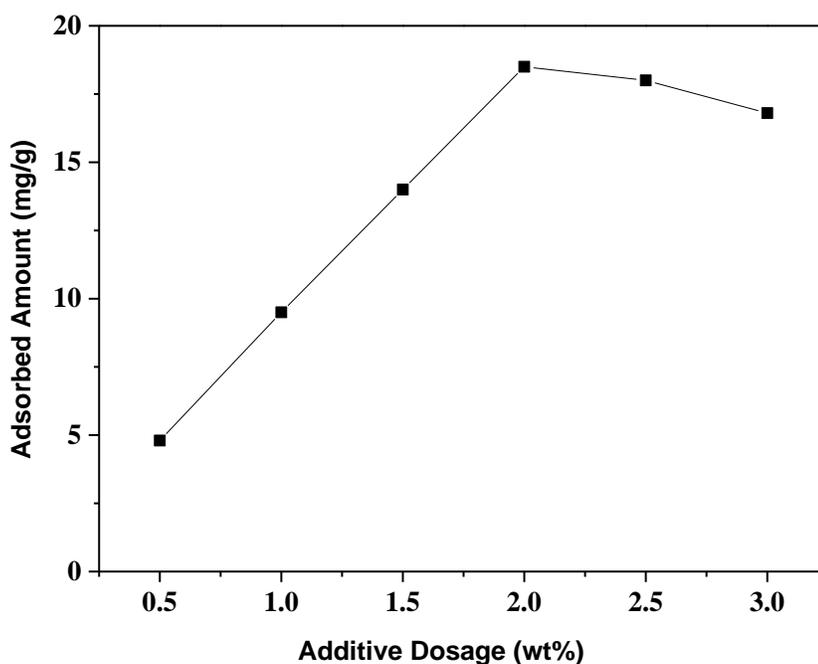


Fig. 7. Impact of lignin-DMC-AA copolymer dosage on fiber absorption

Lignin-DMC-AA Copolymer Retention

Figure 8 depicts the retention rate of paper on the lignin-DMC-AA copolymer sample, calculated as the total amount of lignin-DMC-AA copolymer added. When the dose of lignin-DMC-AA copolymer was less than 2%, the retention of lignin-DMC-AA copolymer was more than 90%. The lignin-DMC-AA copolymer retention continuously decreased with increasing dosage. Further increases up to 6% lignin-DMC-AA copolymer decreased the retention to 56%. When the dosage of the lignin-DMC-AA copolymer was near 1%, the retention of the lignin-DMC-AA copolymer sample was between 81% and 98%.

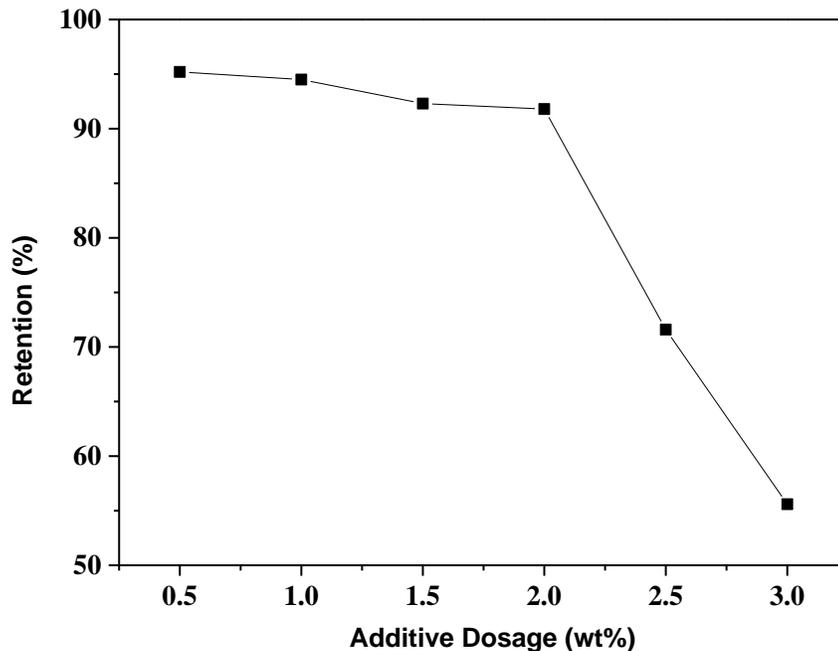


Fig. 8. Influences of lignin-DMC-AA copolymer dosage on the lignin-DMC-AA copolymer retention

CONCLUSIONS

1. In this study, cationic monomer (DMC) and anionic monomer (AA) were grafted onto softwood kraft lignin by free radical polymerization to prepare an amphoteric lignin copolymer.
2. The FTIR, $^1\text{H NMR}$, elemental analysis and charge density analysis methods confirmed that the anion and cation monomers were successfully grafted onto softwood kraft lignin.
3. The grafting ratios of AA and DMC in the lignin-DMC-AA copolymer were 62.4% and 51.3%, respectively. The application of lignin-DMC-AA copolymer as a paper additive enhanced the product's physical properties. At around 2wt% addition of the lignin-DMC-AA, the burst, tensile, and tear indices of paper increased by 48.8%, 71.4%, and 65.1%, respectively
4. The amount of the lignin-DMC-AA absorbed on the fibers was 18.5 mg/g, and its retention was over 90%.

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