# Preparation and Characterization of Lignin-Acrylamide Copolymer as a Paper Strength Additive

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With currently practiced technology, lignin is either incinerated in the recovery cycle of pulping or wasted in wastewater treatment systems, resulting in its underutilization. However, lignin can be converted to value-added products. In this work, the copolymerization of soda lignin (SL) and acrylamide (AM) was carried out using potassium persulphate ($K_2S_2O_8$) as an initiator in an aqueous solution to prepare water-soluble lignin-acrylamide (SL-AM) copolymer as a dry strength additive. The results showed that the optimal copolymerization conditions were 7.5 AM/SL molar ratio, 3.0 wt.% (based on lignin) of $K_2S_2O_8$, 90 °C, and 4 h of reaction time, which resulted in a SL-AM copolymer with 100% solubility at 10 g/L concentration at pH 7 in water, a grafting ratio of 398%, and a molecular weight of $1.94\times10^5$ g/mol. The prepared SL-AM copolymer was characterized by elemental analysis, Fourier transform infrared (FTIR) spectroscopy, $^1$H nuclear magnetic resonance (H-NMR) spectroscopy, and thermogravimetric analysis (TGA). By adding 1.0 wt.% of SL-AM copolymer to the pulp, the tensile, tear, and burst strengths were increased by 23.1%, 22.7%, and 15.2%, respectively, which implies that the resultant copolymer was an effective strength additive for papermaking.

*Keywords: Lignin; Biorefinery; Dry strength additive; Copolymerization; Characterization*

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## INTRODUCTION

Lignin is the second most abundant biopolymer in the world after cellulose; the concentration of lignin in wood ranges from 20% to 30% on a dry matter basis (Ye *et al.* 2013). The worldwide production of industrial lignin has reached several hundred million tons annually (Ye *et al.* 2013). Soda lignin is one of the byproducts of the soda pulping process, which is a popular pulping process in China mainly used for cooking annual crops such as straw, bagasse, and, to some extent, hardwood. Currently, the majority of soda lignin is incinerated as a low cost fuel for the production of steam and energy in pulp mills; furthermore, some soda lignin is landfilled, which leads to environmental pollution and the waste of resources. The utilization of soda lignin as a fuel is not economically feasible (Vishtal and Kraslawski 2011). However, soda lignin has the potential to be used to produce value-added products. The value-added utilization of soda lignin would not only enhance the economic benefits of the soda pulping processes, but will also address the environmental concerns associated with this biomaterial (Vanderklashorst and Strauss 1986; Dizhbite *et al.* 1999; Camarero *et al.* 2014).

In comparison with kraft lignin and lignosulfonates, soda lignin is sulphur-free, and its chemical composition and structure are closer to that of native lignin (Vanderklashorst and Strauss 1987; Vishtal and Kraslawski 2011). It can only dissolve in alkaline aqueous solutions, which limits its end-use applications in acidic or neutral aqueous environments. In addition to the hydrophobic groups or aromatic groups, soda lignin contains hydrophilic groups, such as methoxy and acetyl groups, which are reactive and aid in the production of value-added products (Saarinen *et al.* 2009; Dizhbite *et al.* 2013; Ye *et al.* 2014). The properties of soda lignin can be improved *via* chemical modification occurring on these active groups. One of the chemical modification methods, copolymerization, is widely adopted because its reaction conditions and final product properties are relatively controllable (Marchetti *et al.* 1998; Bhattacharya and Misra 2004). In the past, the copolymerization of lignosulfonate and vinyl monomers using acrylontrile and methyl methacrylate were investigated in aqueous or organic solvents (Meister *et al.* 1984; Ye *et al.* 2014). Among the available water-soluble monomers (such as acrylic acid and hydroxylethyl methacrylate), acrylamide is a relative inexpensive monomer with high reactivity. Its resulting homopolymer, polyacrylamide (PAM), has a versatile application in wastewater (Wang *et al.* 2014). Also, PAM is a common and versatile strength additive used in papermaking processes. In this case, an improvement in dry strength of papers is primarily attributed to the hydrogen bonding development between the amide groups of PAM and the hydroxyl groups of the cellulose fibers (Mihara *et al.* 2008). However, the copolymerization of soda lignin and acrylamide has not been systematically investigated, which was one of the objectives in this study.

Nowadays, dry strength additives are routinely used in papermaking processes for enhancing paper strength, reducing the load to refiners, and compensating for the adverse effects of filler application in paper (Ren and Li 2005; Fatehi and Xiao 2008a; Fatehi *et al.* 2010). The importance of using dry strength additives in papermaking has been comprehensively addressed in the literature (Fatehi and Xiao 2008b; Fatehi 2011). Applying dry strength additives increases hydrogen bonding between the fibers, and the specific bond strength and bond area of the paper can be enhanced (Fatehi and Xiao 2010). The strength properties of chemi-mechanical pulp, *e.g.* high-yield pulp (HYP), are lower than those of chemical pulp, which necessitates the use of a dry strength additive for strength improvement (Liu *et al.* 2010).

The utilization of lignin and its derivatives as strength additives in the papermaking industry have been studied in previous literature (Chen *et al.* 2006; Souguir *et al.* 2012). Cao *et al*. (2010) prepared hydroxyl methylated lignin using ethanol lignin of wheat straw and used this as a strength additive for corrugating medium paper. It was found that at 10% (oven dried weight) dosage of the lignin-based product, the tensile strength of paper increased by 10.3% (Cao *et al.* 2010). Chen *et al*. (2006) also developed a strength additive *via* copolymerizing acrylic acid and hydroxyl methylated lignin, which improved the tensile strength of paper by 18.4 wt.% at 4 wt.% addition. However, there is no report on the application of soda lignin-acrylamide (AM) copolymer as a paper dry strength additive. Therefore, the second objective of this work was to investigate the effect of the lignin-AM copolymer on the strength properties of paper.

In this experiment, the copolymerization of soda lignin and AM was carried out in an aqueous solution in order to prepare the water-soluble lignin-AM copolymer. The effects of the reaction parameters on copolymerization were investigated, and the prepared lignin-AM copolymer was characterized using elemental analysis, Fourier transform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance ($^1$H-NMR), and thermogravimetric analysis (TGA). Also, the prepared lignin-AM copolymer was applied as a dry strength additive in papermaking and its impact on the strength properties of paper were analyzed.

## EXPERIMENTAL

### Materials

Soda lignin (SL) was isolated from black liquor of poplar soda pulping through an acidification process (pH 1.5 using HCl). The precipitated soda lignin was washed thoroughly with deionized water prior to use. Acrylamide (99% purity) was purchased from Sigma-Aldrich (Shanghai, China). The initiator, potassium persulphate ($K_2S_2O_8$; 99.5% purity) and sulfuric acid (reagent grade, 98 wt.%) were obtained from Oumike Agent Company (Jinan, Shandong, China). Alkaline peroxide chemi-mechanical pulp (APMP) was supplied by the Zhong Mao Sheng Yuan Pulp and Paper Company in Shandong Province, China. A dialysis membrane with 1000 g/mol cutoff was purchased from Huamei Biotechnology Company in Beijing, China. Polyacrylamide (PAM) with the molecular weight of $2.5\times10^5$ g/mol was purchased from Jinan Chemicals Company.

### Preparation of SL-AM Copolymer

In this set of experiments, 2.0 g of soda lignin and a required amount of acrylamide were added to a three-neck round-bottom flask with magnetic stirring at 280 rpm, equipped with a reflux condenser and thermometer. Then, 40 mL of deionized water was added to the flask. After 30 min of stirring, the pH of the solution was adjusted to 3.0 using 0.1 M of sulphuric acid. Then, the reactor was immersed in an oil bath in order to maintain a reaction temperature of 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, and 90 °C. Nitrogen was purged into the flask for 20 min, and then the required amount of potassium persulphate was added to the solution to start the copolymerization. A continuous supply of nitrogen was maintained throughout the reaction in order to ensure the absence of oxygen. After completion, the solution was cooled to room temperature by immersing the flask in tap water for 20 min, and then the pH of the reaction solution was adjusted to 1.5 using sulphuric acid. This treatment precipitated the SL-AM copolymer. The suspension was centrifuged at 3000 rpm for 10 min in order to collect the precipitated copolymer and to remove the homopolymer (polyacrylamide; PAM) and unreacted acrylamide monomer. This acidification/centrifugation process was repeated 3 times. Subsequently, the precipitated lignin copolymer was mixed with 100 mL of deionized water, and the pH was adjusted to 7.0 ± 0.2 using 1 M of NaOH solution. Then, the sample was dialyzed using the dialysis membrane for 48 h in order to remove inorganic salt from the copolymer. The deionized water used for dialysis was changed once every 2 h for the first 12 h, and then once every 6 h for the following 36 h. After dialysis, the solution was dried at 105 °C, and the dried sample resulted in the final SL-AM copolymer product.

The copolymerization reaction was repeated using different temperatures (40, 50, 60, 70, 80, and 90 °C), time periods (1, 2, 3, 4, and 6 h), initiator dosages (1.0, 2.0, 3.0, 4.0, and 5.0 wt.% of lignin), and acrylamide to lignin molar ratios (2.5, 5.0, 7.5, 10, and 12.5) in order to optimize the reaction conditions. The yield of SL-AM copolymer was determined using Eq. 1, which was used by Ye *et al.* (2014) and Xu *et al.* (2006):

$$Y\ (\%) = \frac{W_2}{W_0+W_1} \times 100\% \qquad (1)$$

where $W_0$ is the weight of soda lignin used in the reaction (g), $W_1$ is the weight of AM monomer used in the reaction (g), $W_2$ is the weight of the copolymer (g), and $Y$ is yield (wt.%.).

The grafting ratio was determined using Eq. 2,

$$\mathrm{GR}\ (\%) = \frac{71\times \mathrm{V}_1}{14\times 100-71\times \mathrm{V}_2}\times 100\% \qquad (2)$$

where $V_1$ is the nitrogen content measured by elemental analysis (%), 71 is the molecular weight of acrylamide (g/mol), and 14 is the atomic weight of nitrogen (g/mol).

## Molecular Weight Analysis

The molecular weight of soda lignin was determined using gel permeation chromatography (GPC; Agilent 1200, USA), with a refraction index detector (RID), a 10 μm PL-gel, and a mixed-B 7.5 mm ID column, that was calibrated using PL pullulan polystyrene standards (435500, 66000, 9200, and 1320 g/mol MW). A 2.0 mg sample was dissolved in 1.0 mL of tetrahydrofuran, and 20 μL samples were injected into the machine. The column was operated at ambient temperature and eluted with tetrahydrofuran at a flow rate of 1 mL/min.

The molecular weight of the SL-AM copolymer was carried out using a gel permeation chromatography system (Malvern GPCmax VE2001 Module + Viscotek TDA305), with multi-detectors (ultraviolet, refractive index, viscometer, low angle, and right angle laser detectors), Poly Analytic (PA) A206 and A203 columns, and 0.1 M of $NaNO_3$ solution as the eluant (flow rate of 0.7 mL/min). The column temperature was set at 35 °C. Poly(ethylene oxide) was used as the standard. In this set of experiments, 4.0 to 5.0 mg of SL-AM copolymer was dissolved in 1.0 mL of 0.1 M $NaNO_3$ solution, and then 100 μL samples were injected into the machine for analysis.

## Elemental Analysis

The elemental analysis of SL and SL-AM copolymer were determined using an elemental analyzer (Vario EL III, Elementar Analyze System, Germany) *via* the combustion method (Jahan *et al.* 2011). In preparation, the samples were first dried in an oven at 105 °C overnight to remove any moisture. Then, approximately 2.0 mg of each sample was analyzed for carbon, hydrogen, nitrogen, and oxygen content.

## Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of SL and SL-AM copolymer were recorded on a FT-IR spectroscopy (IR Prestige-21, Shimadzu, Japan). The samples were first dried in an oven at 105 °C overnight, and 0.05 g of sample was used for analysis. Each spectrum was recorded in the transmittance mode with 32 scans, in wavenumbers ranging from 400 to 4000 $cm^{-1}$, with a resolution of 4 $cm^{-1}$.

## $^1$H-NMR Analysis

The SL and SL-AM copolymer were analyzed using$^1$H-NMR analysis. Oven-dried samples of SL and SL-AM copolymer were dissolved in $D_2O$ at pH 10.0 and 40 to 50 g/L concentration. The spectra for the samples were recorded with a nuclear magnetic resonance machine (NMR; Bruker AVANCE II 400 MHz, Billerica, MA, USA) at room temperature, with a 45° pulse and a relaxation delay time of 1.0 s.

### Thermogravimetric Analysis (TGA)

Thermogravimetric analyses of the SL and SL-AM copolymer were performed using a thermogravimetric analyzer (Q50, TA Instruments, New Castle, DE, USA) in order to characterize the decomposition profiles of these two samples. The samples were heated from 35 to 900 °C at the heating flow rate of 20 °C/min in nitrogen at the flow rate of 100 mL/min.

### Handsheet Preparation and Analysis

In this set of experiments, handsheets (60 g/m$^2$) were prepared using a TAPPI standard handsheet machine (PTI, Germany) with APMP pulp. Prior to the sheet preparation, the SL-AM copolymer was added into the pulp slurry at 1.0% consistency, and stirred for 5 min at 500 rpm. Afterwards, the pulp slurry was placed in the handsheet former in order to prepare handsheets according to the TAPPI T205 om-88 (1995) (TAPPI 1996). After drying, the tensile, burst, and tear strengths, brightness, as well as the internal bonding strength (*i.e.* Scott type) of the handsheets, were measured according to the TAPPI T494 om-87 (1988), T403 om-91 (1991), T414om-82 (1988), T452om-92 (1992) and T569 om-14 (1996) standards, respectively (TAPPI 1996).

## RESULTS AND DISCUSSION

### Effect of Reaction Conditions on the Yield and Grafting Ratio

The copolymerization of poplar soda lignin and AM was carried out using free radical polymerization. The process used potassium persulphate as the initiator in an aqueous solution, utilizing heterogeneous reaction. Figure 1 shows the reaction scheme of lignin and AM. Potassium persulphate initially produces sulfate radicals in the reaction solution. The sulfate radicals then form phenoxy radicals, which serve as reaction sites on the lignin backbone. These free radical sites then react with AM monomers or propagated monomers to form copolymers. Also, the sulfate radicals can initiate the homopolymerization of AM, resulting in polyacrylamide (PAM), produced *via* side reactions (Fig. 1). To minimize the side reactions and understand how the reaction conditions affect the copolymerization of SL with AM, the effects of the reaction parameters on the yield of the SL-AM copolymer and grafting ratio were investigated.

### Effect of AM Dosage on Copolymerization

Figure 2 shows the effect of the AM/SL molar ratio on copolymerization. The grafting ratio and the yield of SL-AM copolymer were increased by 350% and 70%, respectively, at an AM/SL molar ratio of 7.5. At an AM/SL molar ratio of greater than 7.5, the increases in the grafting ratio and copolymer yield were not remarkable. This may have been because higher concentrations of AM can promote the reaction of soda lignin with AM. However, when the ratio of AM/SL was greater than 7.5, more AM compounds were probably homopolymerized to form PAM, thus competing with the copolymerization reaction. Fang *et al.* (2009) observed that the homopolymerization of acrylamide became dominant when the AM/lignin molar ratio was higher than 7.7 in the copolymerization of enzymatically hydrolyzed lignin and AM in NaOH solution.

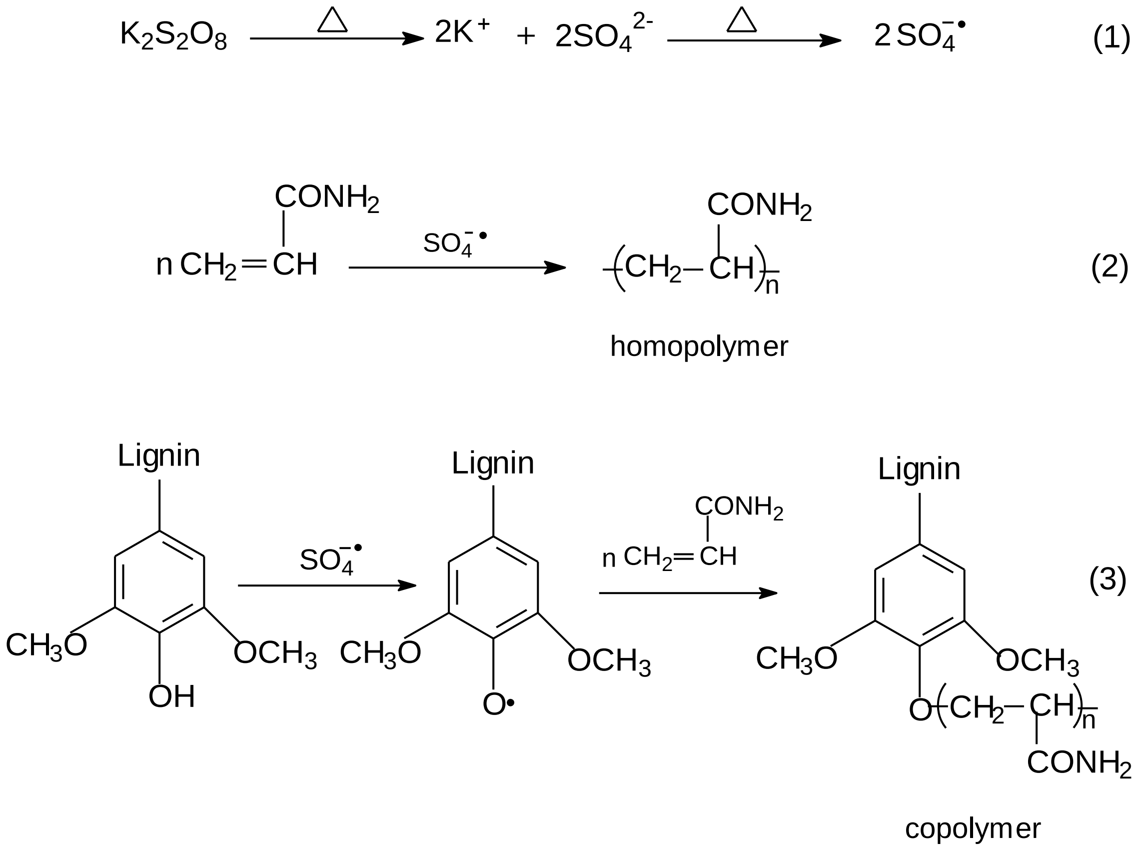

**Fig. 1.** Copolymerization of soda lignin and acrylamide

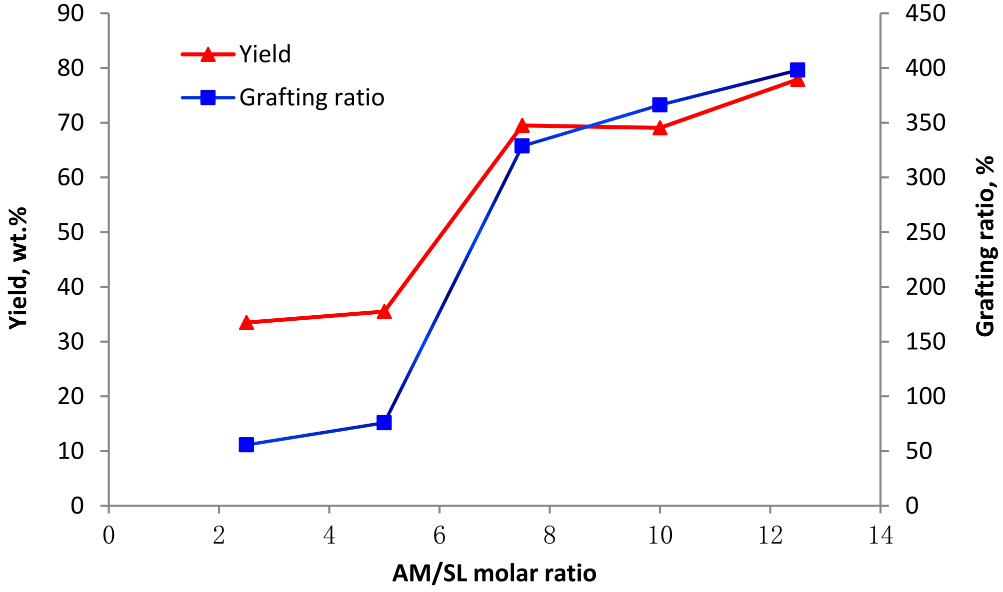

**Fig. 2.** Effect of the AM/SL molar ratio on copolymerization (conditions: initiator 3.0 wt.% based on lignin, pH 3.5, 3 h, and 80 °C)

## Effect of Reaction Temperature on Copolymerization

The copolymerization reaction was conducted at various reaction temperatures ranging from 40 °C to 90 °C, and the results are presented in Fig. 3. The yield and grafting ratio increased dramatically with the increase in reaction temperature from 40 °C to 60 °C. This was attributed to the increased forming rate of initiator radicals and its contribution to the initiation of copolymerization at high temperatures (Ibrahim *et al.* 2005). At temperatures above 60 °C, the yield of copolymer and the grafting ratio increased insignificantly, which was attributed to the fact that at high temperatures (>60 °C), the termination reaction increased and the copolymerization efficiency decreased, as reported by Naguib (2002). Figure 3 also shows that at 90 °C, the grafting ratio and copolymer yield reached their maximum.

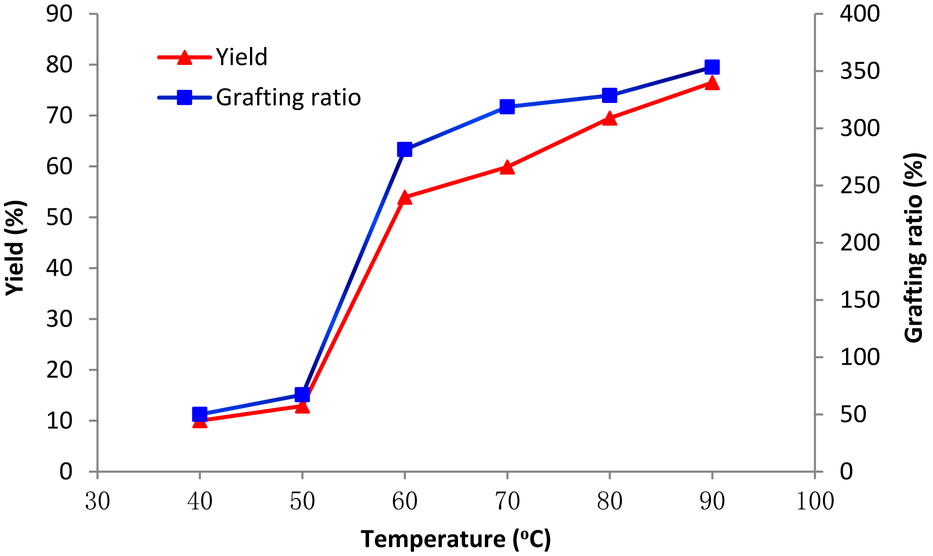

**Fig. 3.** Effect of reaction temperature on the copolymerization (conditions: molar ratio of AM/SL 7.5, initiator 3.0 wt.% based on lignin, pH 3.5 and 3 h)

## Effect of Reaction Time on Copolymerization

The effects of reaction time on the yield of copolymer and the grafting ratio are shown in Fig. 4. It can be seen that the yield and grafting ratio increased rapidly as the reaction time was increased from 1 h to 4 h. When the reaction time exceeded 4 h, the further increase in the grafting ratio and yield became unremarkable. The initial increase in the grafting ratio and yield was attributed to the increase in the number of active sites formed on the SL and the extension of the propagation of copolymer with prolonging time (Ibrahim *et al.* 2005). However, a retardation of AM diffusion into lignin particles may have occurred after some of the monomers were grafted onto the SL surface, which decreased the reaction rate (Ibrahim *et al.* 2005). In addition, the mutual annihilation of growing grafted chains, such as the termination reactions between lignin macro radicals, may have also hampered the copolymerization process (Behari and Pandey 2006; Fang *et al.* 2009).

## Effect of Initiator Dosage on Copolymerization

To investigate the effect of initiator dosage on the yield of copolymer and the grafting ratio, the initiator dosage was varied from 1.0 wt.% to 5.0 wt.% based on the lignin concentration, and the results are presented in Fig. 5.

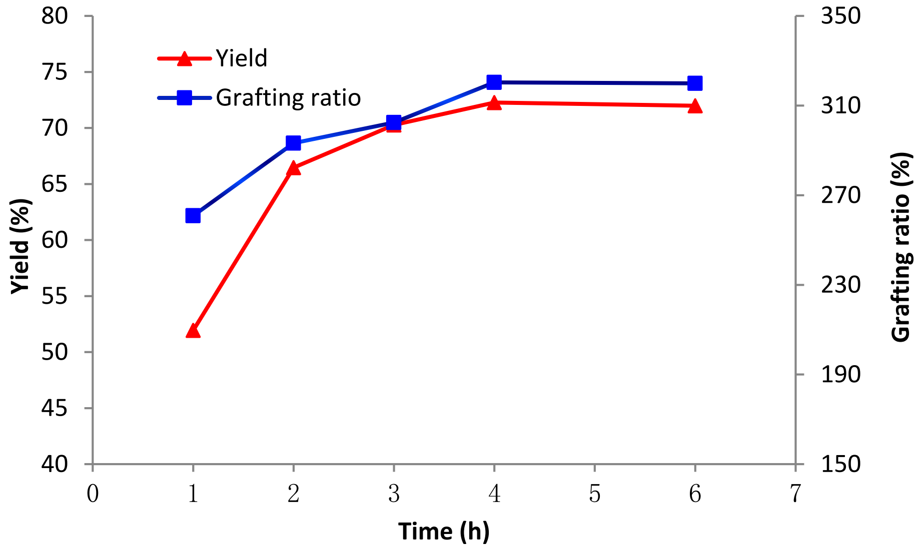

**Fig. 4.** Effect of the reaction time on copolymerization (conditions: molar ratio of AM/SL 7.5, initiator 3.0 wt.% based on lignin, pH 3.5, and 80 °C)

In this copolymerization reaction, $K_2S_2O_8$ acts as an initiator, providing free radicals that create phenoxyl free radicals on the backbone of SL, which the acrylamide or polyacrylamide chains are grafted from (Chen *et al.* 1980). Figure 5 shows that the yield of the copolymers and grafting ratios increase dramatically with the increase in the initiator dosage from 1.0 wt.% to 3.0 wt.%. This increase was attributed to the formation of more radicals at a higher dosage (Chen and Kokta 1982). When the dosage was higher than 3.0 wt.%, the yield and grafting ratio decreased gradually. This was ascribed to the increase in the rate of termination, particularly *via* bimolecular collisions between two SL macro radicals species, which reduced the copolymerization rate, as observed by Chen and Kokta (1982). Also, at a high dosage of initiator, the formation of the homopolymer, PAM, was more pronounced, as previously stated by Fang *et al.* (2009). In other words, the yield of copolymer and the grafting ratio both reached their maximum at the initiator dosage of 3.0 wt.%.

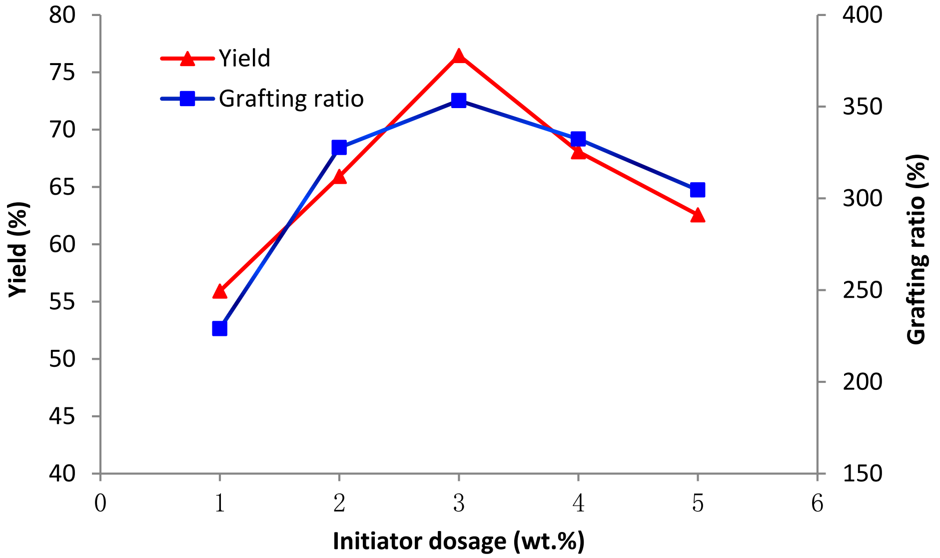

**Fig. 5.** Effect of initiator dosage on the copolymerization (conditions: molar ratio of AM/SL 7.5, 3 h, pH 3.5, and 80 °C)

Based on the results described in previous sections, the optimal conditions for SL-AM copolymer production was a AM/SL molar ratio of 7.5, $K_2S_2O_8$ at 3.0 wt.% based on lignin, 90 °C, and 4 h. The SL-AM copolymer, which was prepared under optimal conditions, was used for elementary analysis, FTIR, NMR, and TGA. This SL-AM copolymer had a grafting ratio of 398% and a yield of 80%. The molecular weight (MW) of the SL-AM copolymer reached $1.94 \times 10^5$ g/mol, which was notably higher than that of unmodified SL (6,459 g/mol). Also, it was found that the SL-AM copolymer prepared under optimal conditions was water soluble at 10 g/L concentration and pH 7.

## Characterization of SL-AM Copolymer

### *Elemental analysis*

The elemental analyses of SL and the SL-AM copolymer, which were produced under the optimal reaction conditions, were carried out, and the carbon, hydrogen, nitrogen, and oxygen content of samples are listed in Table 1. The SL showed a negligible amount of nitrogen (0.03 wt.%). Compared with SL, the SL-AM copolymer showed a considerable amount of nitrogen, indicating a high content of AM in the backbone of the soda lignin. Based on the elemental analysis, the $C_9$ formulas of SL-AM copolymer were calculated and listed in Table 1. The formulas of SL and SL-AM copolymers showed that the nitrogen content increased from 0.004 to 2.82, along with the hydrogen content; however, the oxygen content was slightly decreased, which occurred because of the low amount of hydrogen and high amount of oxygen in the AM segment of the SL-AM copolymer. Therefore, based on this analysis, the copolymerization of AM and SL successfully altered the elemental components of SL.

**Table 1.** Elemental Analysis of SL and SL-AM Copolymers

| Polymer | C(wt.%) | H(wt.%) | N(wt.%) | O(wt.%) | Molecular formula |
|---|---|---|---|---|---|
| SL | 54.39 | 5.726 | 0.032 | 39.25 | $C_9H_{11.37}O_{4.87}N_{0.004}$ |
| SL-AM | 44.89 | 8.113 | 16.39 | 30.61 | $C_9H_{19.52}O_{4.60}N_{2.82}$ |

## FTIR of the SL-AM Copolymer

The FTIR spectra of the SL and SL-AM copolymers are shown in Fig. 6. It was observed that both the SL and SL-AM copolymers exhibited a broad band around 3400 $cm^{-1}$, which was assigned to the O-H stretching absorption in the phenolic and aliphatic compounds. A band identified around 2900 $cm^{-1}$ was assigned to the C-H stretching in the methyl groups (El Mansouri and Salvadó 2007). In the spectrum of SL, the bands at 1593, 1496, and 1425 $cm^{-1}$ corresponded to the aromatic skeletal vibration of SL (Cazeils *et al.* 2012). Two absorption bands centering around 1330 and 1116 $cm^{-1}$were assigned to C-O stretch and C-H stretch of syringyl unit, respectively, illustrating that SL is a hardwood lignin.

In the case of SL-AM copolymer, two peaks were observed at 1676 and 1617 $cm^{-1}$, which were assigned to the carbonyl groups and C-N stretching vibration of the amide groups, respectively (El-Zawawy and Ibrahim 2012). In addition, the characteristic bands for aromatic skeleton vibration of SL were also observed in the spectrum of SL-AM copolymer, showing that the SL was successfully copolymerized with AM.

Figure 6 depicts the relative intensity of the band at 1030 $cm^{-1}$, which belongs to non-etherified phenolic hydroxyl groups. This implied that then non-etherified phenolic hydroxyl groups are weaker in the SL-AM copolymer than in SL, suggesting that lignin participated in the copolymerization reaction through its active phenolic hydroxyl group, as also stated by Ye *et al.* (2014).

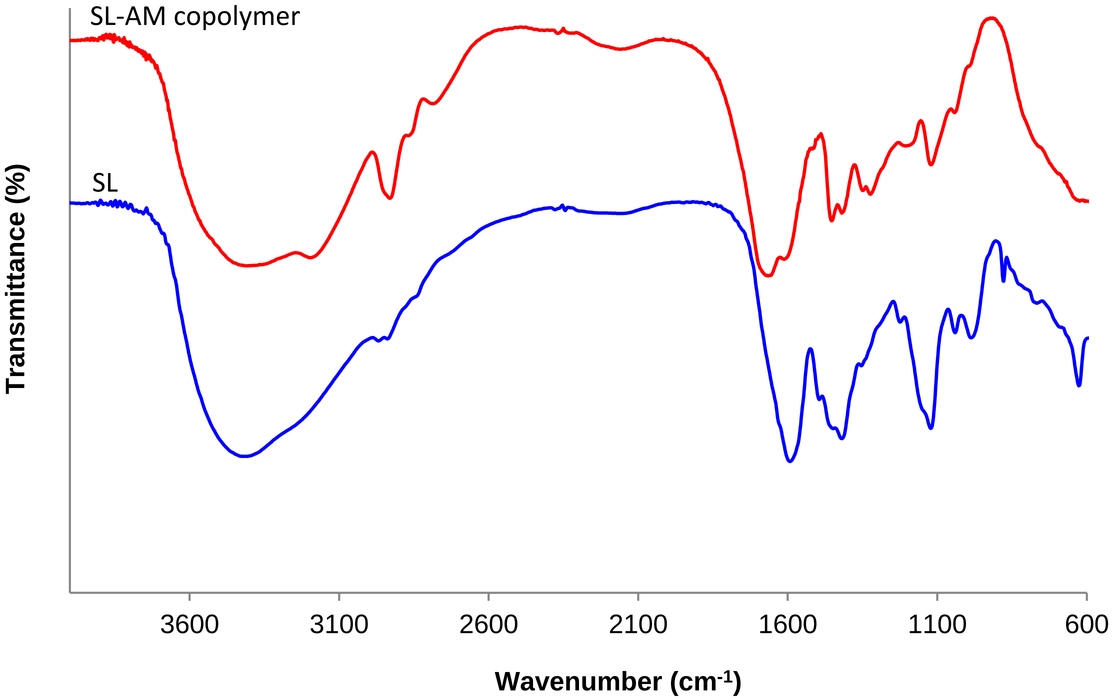

**Fig. 6.** FTIR spectra of SL and SL-AM copolymer

## $^1$H-NMR of the SL-AM Copolymer

Figure 7 shows the$^1$H-NMR spectra of SL and SL-AM copolymer. In the spectrum of SL, the peaks at 7.70, 7.60, and 6.90 ppm were attributed to aromatic protons; the peak at 6.15 ppm was attributed to the $H_\beta$ of the cinnamyl alcohol unit; the peak at 5.75 ppm was attributed to the $H_\alpha$ in β-5 structures; the peak at 4.0 ppm was attributed to hydroxyl protons; the peaks at 3.70 to 3.30 ppm were attributed to protons in the methoxyl groups of lignin; and the peak at 3.15 ppm was assigned to the methylene protons in the β-β structure (Lundquist 1981; Runge and Ragauskas 1999; Nagy *et al.* 2010; Hu *et al.* 2014). Peaks appearing at 4.5 to 4.9 ppm were assigned to the peaks from solvent $D_2O$.

In the SL-AM copolymer spectrum, two additional peaks at 1.6 and 2.2 ppm were observed, which were not present in the SL spectrum. These two peaks were assigned to the protons of $C_\alpha$ and $C_\beta$, respectively, connecting the amide groups of the copolymer (Song *et al.* 2007; Yang *et al.* 2010). The presence of these two peaks indicated that amide groups were introduced into the backbone of SL and that the copolymerization reaction was successfully performed.

Also, a peak at 4.30 ppm was observed in the spectrum of the SL-AM copolymer, which was absent in that of the SL spectrum. This peak was assigned to the protons connecting $-CH_2-$to the aromatic structures through ester bonding ($-CH_2-O-C_6H_5$) (Xiong *et al.* 2003; Kang *et al.* 2014). This confirms that the phenolic hydroxyl groups were located in the active sites, participating in the copolymerization reaction, which was consistent with the FTIR results.

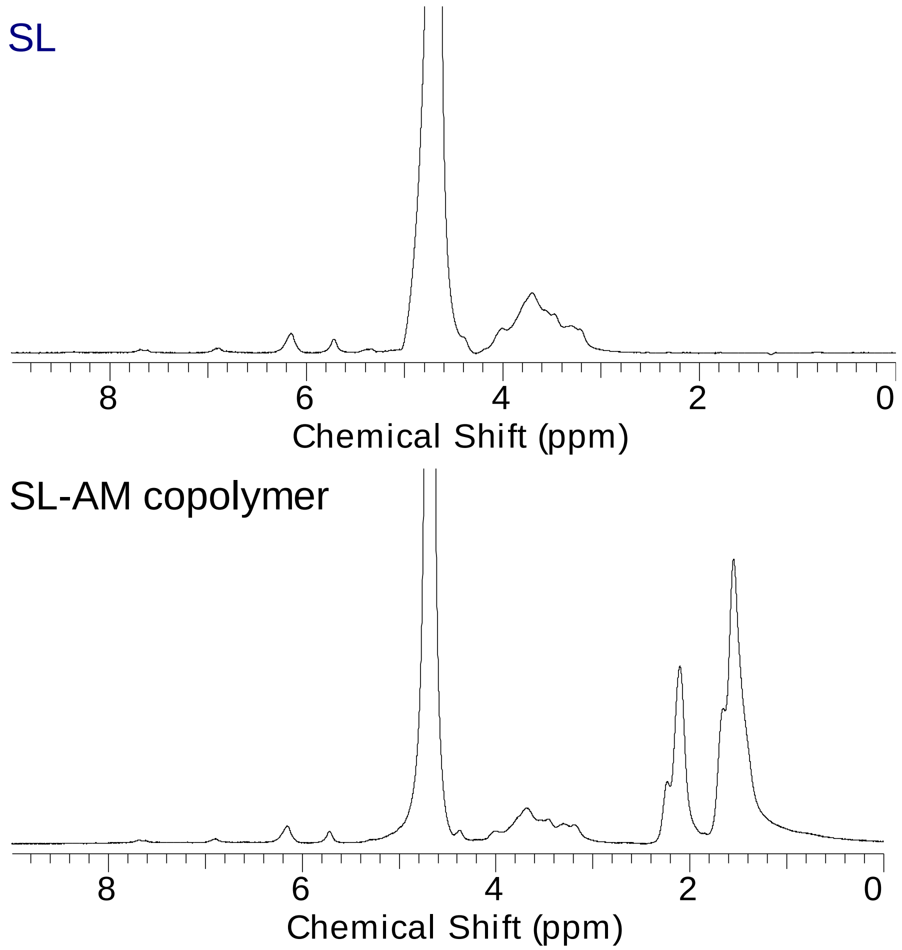

**Fig. 7.** $^1$H-NMR spectra of SL and SL-AM copolymer

## Thermogravimetric Analysis (TGA)

The thermogravimetric analysis of SL and SL-AM copolymer is shown in Fig. 8. The weight loss behavior of both samples depicted two or three steps of degradation. The first decomposition step of SL was recorded in the temperature range of 35 to 165 °C, with a 6.7 % weight loss corresponding to water evaporation (*i.e.*, moisture loss). The second decomposition step occurred in the temperature range of 165 to 496 °C, with 40.2% weight loss, and was attributed to the fragmentation of the inter-unit linkages of SL (Elsaied and Nada 1993). The main decomposition temperature was at 347 °C.

The first decomposition step of the SL-AM copolymer occurred between the temperature ranges of 35 to 223 °C, with 11.7% weight loss attributed to the elimination of moisture. The second decomposition step occurred in the range of 223 to 313 °C, with 12.1% weight loss attributed to the decomposition of the AM segment in the copolymer (Sahoo *et al.* 2005; Yang 1998). The third decomposition step occurred in the range of 313 to 507 °C, with 55.1% weight loss corresponding to the decomposition of the SL-AM copolymer backbone (Yang *et al.* 2007; Dominguez *et al.* 2008). The main decomposition temperature for the SL-AM copolymer was 397 °C, which was higher than that of SL (347 °C). This analysis showed that when SL-AM copolymer is exposed to heat, the PAM segment in the copolymer degrades at lower temperatures first, which probably prevents heat transfer to the lignin backbone. When the temperature was greater than 313 °C, decomposition, condensation, and secondary cracking of the backbone of the SL-AM copolymer likely occurred (Dominguez *et al.* 2008). Based on the results, one can conclude that the SL-AM copolymer was stable at temperatures lower than 223 °C, which was greater than the temperature of 120 to 130 °C used for the drying stage of papermaking. Therefore, this copolymer could be used as a paper strength additive, and will not decompose during the drying stage of the papermaking process. In addition, it is observable that a part of the SL-AM copolymer remained as ash after incinerating at 900 °C.

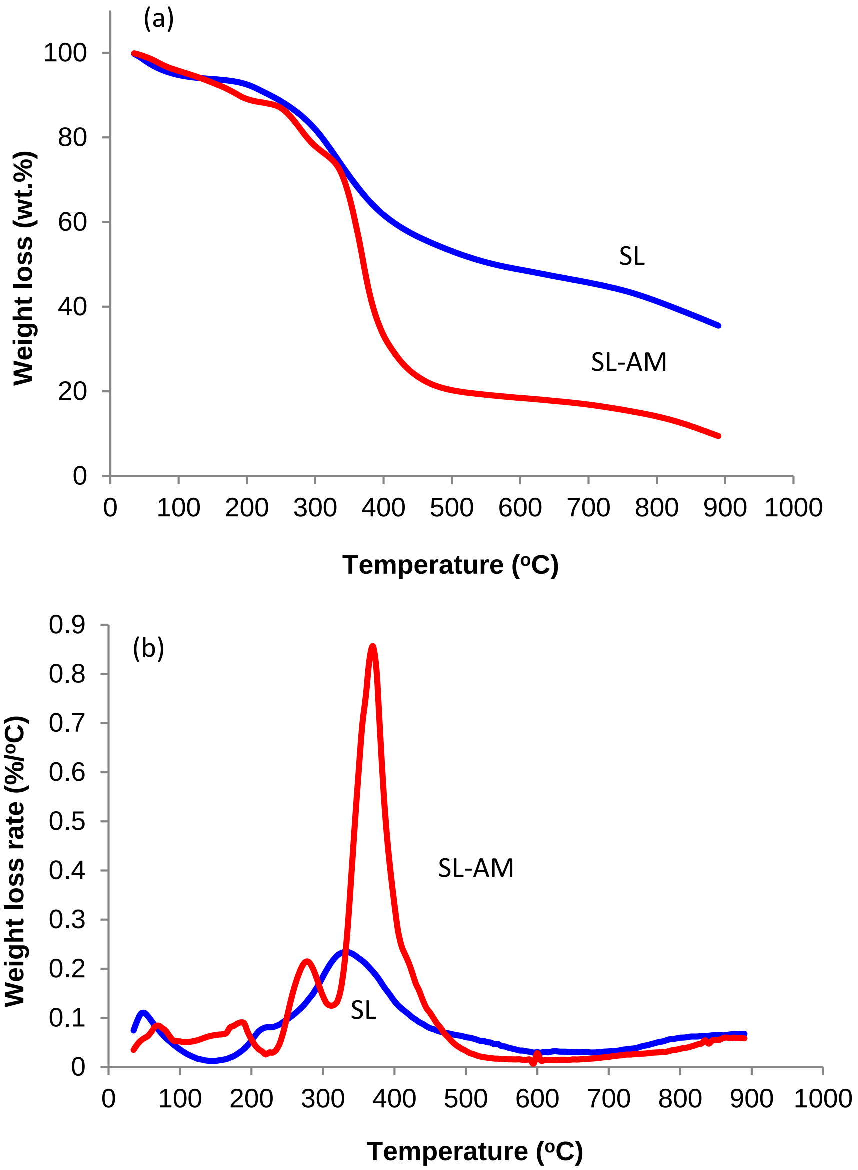

**Fig. 8.** (a) Weight loss and (b) weight loss rate of SL and SL-AM copolymer

## Paper Strengthen Performance of SL-AM Copolymer

Figure 9 shows the changes in tensile, tear, and burst indices of papers, as well as brightness, as a function of the dosage of SL-AM copolymer. When the dosage of SL-AM copolymer increased from 0 % to 1.0 %, the tensile, tear, and burst indices increased significantly. At 2 wt.% dosage, the maximum increases of 24.2 %, 29.4 %, and 15.9 %, were obtained for tensile, tear, and burst indices, respectively. These results show that the

SL-AM copolymer would be an effective dry strength additive for papermaking. At a 2.0% dosage, the brightness of handsheets declined from 65.6% ISO to 65.4% ISO. Further increases in the dosage of SL-AM copolymer led to a slight decrease in the tear index and brightness of the handsheets.

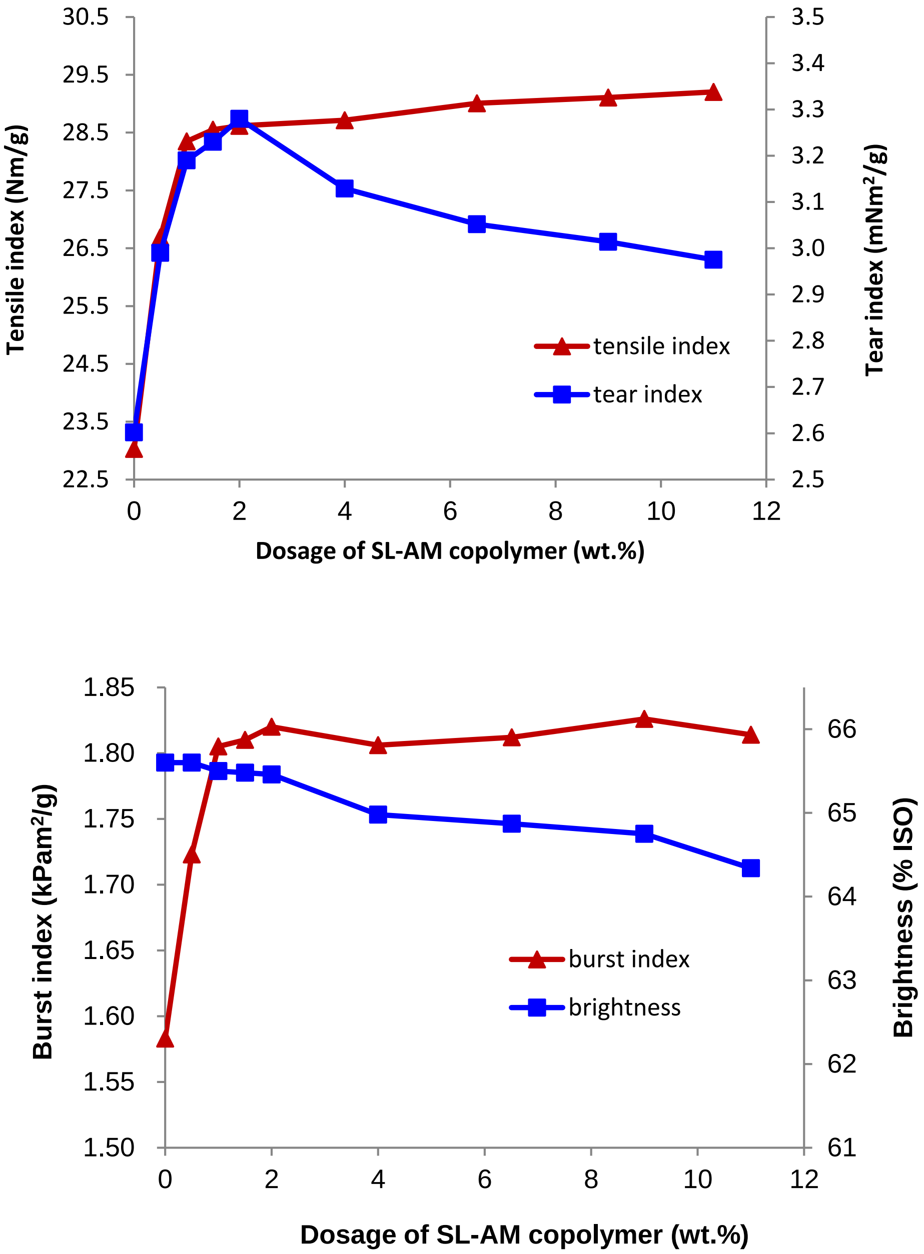

**Fig. 9.** Paper properties as function of dosage of SL-AM copolymer

Figure 10 shows the mechanical properties of papers in which SL-AM or commercial PAM was used as a strength additive at 1 wt.% dosage. As can be seen, the SL-AM copolymer improved the properties more significantly than did PAM. These results clearly show that SL-AM was a more effective strength agent than PAM. However, more extensive analysis is needed to determine factors that led to the better results for SL-AM copolymer.

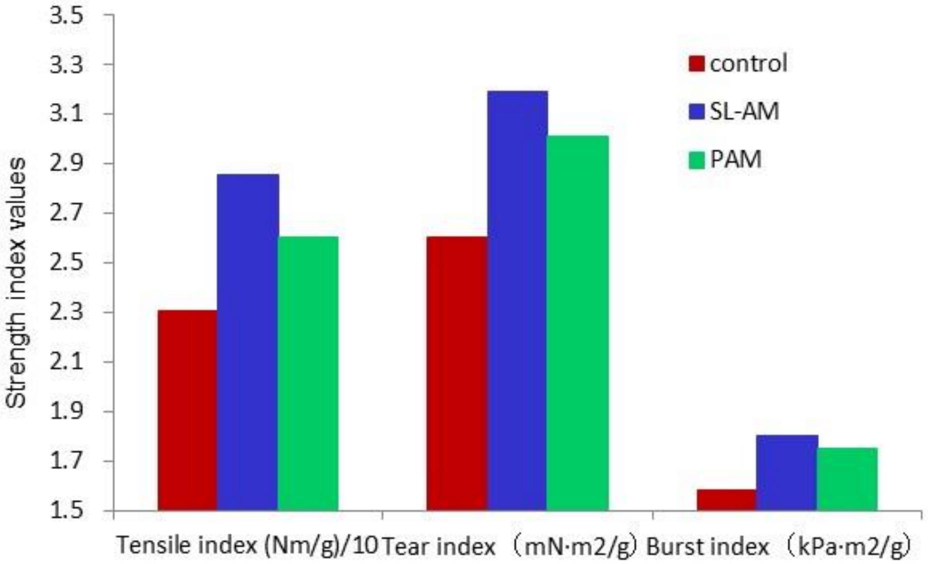

**Fig. 10.** Paper properties in which SL-AM copolymer or PAM was used as a strength agent at 1 wt.% dosage. The actual tensile indices can be calculated by multiplying the values of tensile index in this figure by 10.

The increase in the strength of papers was mainly attributed to the formation of hydrogen bonding between the amide groups of SL-AM copolymer and cellulose fibers. Figure 11 illustrates the bridging mechanism of SL-AM copolymer on fibers. The hydrogen bonding development of SL-AM and cellulose fibers would facilitate the adsorption of SL-AM copolymer on fibers. If parts of SL-AM copolymer are adsorbed on two adjacent fibers (*i.e.* crossing points of fibers in Fig. 11), the AM segment of the SL-AM copolymer would then act as a bridge and reinforce the bonding between the fibers (Maximova *et al.* 2001). Most probably, SL-AM copolymer would evenly adsorb on fiber surface. However, only the SL-AM copolymers that impacted the strength improvement of papers are shown in Fig. 11 rather than SL-AM copolymers that are adsorbed elsewhere.

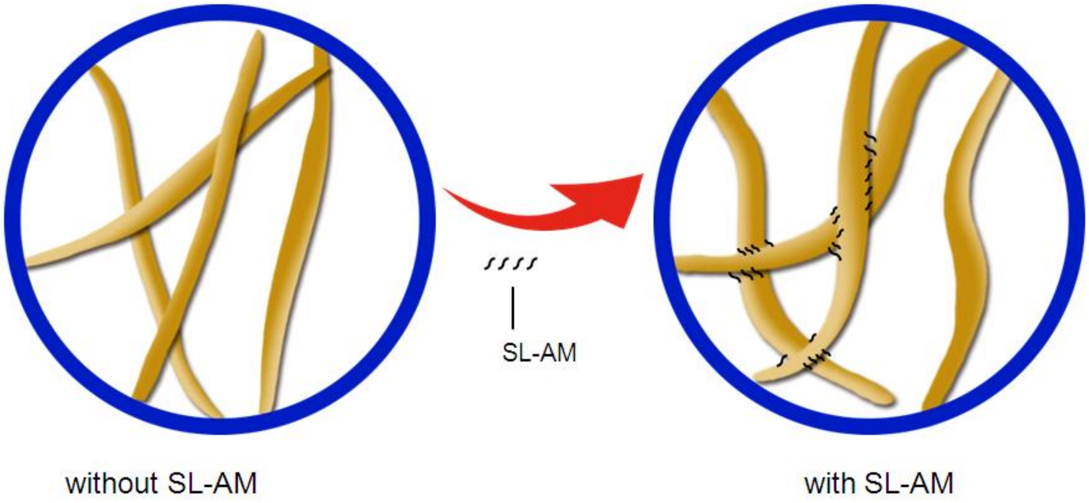

**Fig. 11.** Bridging of fibers by SL-AM copolymer

Table 2 lists the internal bonding strength of papers in which SL-AM or PAM was used as a strength additive. Interestingly, the internal bonding strength of papers was increased from 187 J/m$^2$ to 265 J/m$^2$ at 1 wt.% SL-AM dosage or to 289 J/m$^2$ at 2 wt.% SL-AM dosage. The increase in the internal bonding strength was less significant for the papers in which PAM was the strength additive, which clearly showed that SL-AM was more effective than PAM in increasing the internal bonding strength of the papers.

**Table 2.** Internal Bonding Strength of Papers in which SL-AM or PAM was a Strength Additive

| Polymer | Control | SL-AM | | PAM | |
|---|---|---|---|---|---|
| Dosage, wt.% | 0 | 1.0 | 2.0 | 1.0 | 2.0 |
| Internal bonding strength (J/m$^2$) | 187 | 265 | 289 | 247 | 276 |

The results in this paper clearly showed that the SL-AM copolymer can be used as an effective dry strength additive in papermaking applications when the brightness of paper is less important, *e.g.* corrugated medium and container board.

## CONCLUSIONS

1. The preparation and the application of SL-AM copolymer was studied in this work. The optimal conditions for the copolymerization of SL and AM were a AM/SL molar ratio of 7.5, $K_2S_2O_8$ at 3.0 wt.% based on lignin, 4 h reaction time, and 90 °C. This optimal condition resulted in SL-AM copolymer with a yield and the grafting ratio of 80 % and 398 %, respectively.
2. Elemental analysis, FTIR spectroscopy, NMR, and TGA results confirmed that the copolymerization reaction was successful. The TGA analysis also showed that the SL-AM copolymer may not decompose in the drying stage of the papermaking process.
3. The SL-AM copolymer enhanced the strength properties of paper considerably. At a 1.0 wt.% dosage of the SL-AM copolymer, the tensile, tear, and burst indices of the papers increased by 23.1%, 22.7%, and 15.2%, respectively; however, the brightness minimally declined from 65.6% ISO to 65.5% ISO.

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