

Preparation of Aminated Lignin through Etherification and Amination

ChangZhou Chen, BingXin Wang, YanRu Zhang, Ting Shi, Jun Liu, XiLuan Wang*, YongMing Fan

College of Material Science and Technology, Beijing Forestry University, Beijing, 100083, China



ChangZhou Chen, PhD candidate;
E-mail: ccz1988521@163.com

Abstract: A new method for the preparation of aminated lignin (AEL) through etherification and amination reaction was presented. Chlorine atoms were firstly introduced into lignin through its etherification with epichlorohydrin. Then, hydrophilic amine groups were grafted to the modified lignin structure through amination with ethylenediamine to obtain AEL. Subsequent acidification of AEL led to the ionized aminated lignin (IAEL). The results of our analyses showed that the nitrogen content of AEL was 6.9%. Foaming and emulsifying experiments indicated that AEL had better foamability and emulsifying properties than IAEL. Surface tension tests showed that AEL and IAEL had similar critical micelle concentration (CMC). However, IAEL had lower surface tension (36.33 mN/m) than AEL (42.89 mN/m) at CMC. These results demonstrate the promising applicability of AEL as an emulsifier and that of IAEL as feedstock in the production of detergent and dispersant.

Keywords: lignin; etherification; amination; epichlorohydrin; ethylenediamine



*Corresponding author:
XiLuan Wang, PhD, lecturer;
research interests: the synthesis
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materials;
E-mail: wangxiluan@bjfu.edu.cn

1 Introduction

Lignin, the most abundant aromatic renewable resource, is green and low-cost feedstock for biofuels, chemicals and biomaterials^[1-2]. As a polyfunctional substance, lignin contains hydroxyl, carbonyl, carboxyl and methoxy groups. It is an exciting candidate for chemical modification to produce new materials and chemicals because of its plentiful active functional sites. The conversion of lignin into lignin-based chemicals and materials can not only reduce the consumption of petrochemical resources but also extend the value-added applications of lignin in the future. Therefore, a number of methods have been proposed to transform lignin into various lignin-based products, mainly including lignin-phenol-formaldehyde resins^[3-4], lignin-based polyurethane^[5-6], lignin-based epoxy resins^[7-8], and lignin surface-active substances (surfactants)^[2]. Three types of water-soluble lignin derivatives (anionic,

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cationic and non-ionic forms) with good surface activity have attracted researchers' attention. However, exploitation of the cationic and non-ionic lignin derivatives has been scarcely reported in past decades.

Sulfonation is the most widely used method to transform lignin into a good water-soluble anionic surfactant^[9-10]. In addition to the traditional applications (e.g., oil recovery sacrifice agent, pesticide and dye dispersant), anionic lignin surfactants have been used for fabricating high-quality graphene^[11-12]. Recently, non-ionic amphiphilic lignin derivatives have been prepared by introducing hydrophilic polyethylene glycols (PEGs) into lignin through the reaction between phenolic hydroxyl lignin and PEG with diglycidyl (PEGDE) and monoglycidyl (EPEG) groups or with PEG-chlorohydrin^[13-14]. In a previous study^[15], we prepared non-ionic amphiphilic lignin derivatives that not only displayed great surface activity and emulsifying properties but also significantly improved enzymatic hydrolysis and bioethanol production^[16-18] by means of the reaction of epoxy lignin monomer with PEGs. Cationic lignin-based derivatives with amino groups are synthesized mainly based on the Mannich reaction or through epoxidation followed by amination^[19]. Aminated lignin presents good surface activity and emulsifying properties, and as an asphalt emulsifier, it has broad application prospects^[20-21]. Besides their usage as surfactants, cationic lignin-based derivatives have potential value-added applications as polycationic materials and low-release fertilizers^[22], heavy-metal adsorbent^[23-24], and negatively charged pollutants or flocculants^[25-26] because of their abundant active coordinative groups. However, as the Mannich reaction and the epoxidation followed by amination approaches involve the utilization of excess concentrated H_2SO_4 (98%, w/w) and concentrated sodium hydroxide solutions (50%, w/w), the commercialization of cationic lignin-based derivatives is limited.

In this work, a new method to prepare aminated lignin through etherification followed by amination, to avoid the application of concentrated acids and alkali, was presented. In this case, after the

introduction of halogen atoms in lignin through its reaction with epichlorohydrin (ECH) catalyzed by tetrabutylammonium bromide, lignin was aminated with ethylenediamine to introduce hydrophilic amine groups in its structure. Further neutralization of this compound with hydrochloric acid solution led to a cationic lignin surfactant. The structure of lignin derivatives and some of their properties such as foamability, emulsification, and surface activity were investigated.

2 Experimental

2.1 Materials

Pure lignin (AL) from corncob was provided by Shandong Longlive Bio-technology Co., Ltd., China. The content of aliphatic OH, phenolic OH, COOH, and total OH of the lignin were 2.26, 3.53, 2.24, and 8.03 mmol/g lignin, respectively^[15]. Analytical grade (AR) of epichlorohydrin (ECH), tetrabutyl ammonium bromide (TBAB), ethylenediamine, and ethyl acetate were supplied by Sinopharm Chemical Co., Ltd., Beijing.

2.2 Modification of lignin with ECH

First, 50.0 g of AL and 15.0 g of TBAB were slowly added into 400 mL of ECH in a 1000 mL three-necked flask at room temperature under mechanical stirring. The reaction was run by heating the obtained mixture to 90°C for 6 h. After reaction, the mixture was vacuum evaporated to 50 mL. The resulted concentrate was precipitated into 500 mL of anhydrous ethanol, filtered, and dried in ventilation at room temperature to afford an ECH-modified lignin sample, named as EL.

2.3 Preparation of aminated lignin and ionized aminated lignin

A 10.0 g sample of EL was dispersed evenly and dissolved into 100 mL of ethylenediamine in a 250 mL round-bottom flask under stirring; then, the reaction was run at 80°C for 6 h. After the reaction, the mixture volume was concentrated to 20 mL under reduced pressure, and the resulting concentrate was precipitated in 50 mL of ethyl acetate solution to obtain the aminated

lignin, named as AEL. Finally, an aqueous solution of 0.2 g/mL of AEL was prepared by dissolving 10.0 g of AEL in 50 mL of deionized water. The as-obtained solution was adjusted to pH value 2 using 1 mol/L HCl solution, and then freeze-dried at -60°C for 36 h to produce the ionized aminated lignin, named as IAEL.

2.4 Characterization

The FT-IR spectra, NMR spectra, and elemental analysis were carried out as previously reported^[27].

The surface tension of the product solution was measured at room temperature using an automatic surface tension meter (QBZY-2, Shanghai Fangrui Instrument Co., Ltd.). Deionized water (surface tension of 72.12 mN/m) was employed as a reference.

The emulsification test was carried out by mixing 6 mL of a series of aminated lignin or cationic aminated lignin solutions with different concentrations in an equal volume of *n*-hexane using a vortex mixer at 3000 r/min for 10 min, and allowing them to stand for 24 h. The heights of water, oil, and emulsions were measured at equilibrium. The physical size of the emulsion droplets in the emulsion layer was observed with a Lecia DM2500 optical microscope.

The foaming capacity test was performed by adding 5 mL of the product solution in a 25 mL test tube with a stopper, and shaking 2 times/s for 2 min each. The initial volume of the foam was recorded when the oscillation was stopped, and named as V_1 . After 20 min, the final volume of the foam was recorded as V_2 . The foaming stability was estimated by the ratio of the volume of the initial foam to that of the final foams (V_1/V_2).

3 Results and discussion

3.1 Preparation of AEL and IAEL

Typically, AL is insoluble in neutral water and most of organic solvents because of its low hydrophilicity and

lipophilicity, which is sometimes not convenient for the chemical modification of lignin. To modify lignin, ECH was used as both the solvent and reactant. The synthesis route of the aminated lignin, AEL, is shown in Fig.1. The TBAB-catalyzed reaction^[28] between the epoxide and the hydroxyl substituents in lignin led to the incorporation of chloropropanol moieties into the lignin structure. EL was then obtained as a yellow-brown powder that precipitated from anhydrous ethanol, and was found to completely dissolve in dichloromethane. After etherification with ECH, the reaction of EL with ethylenediamine, through its amino group, produced AEL as a precipitate from the ethyl acetate solution, which was added to remove the excess of ethylenediamine. The nitrogen content of the modified lignin increased to 6.9% in AEL. The ionized aminated lignin, IAEL, was directly obtained by acidification of AEL with hydrochloric acid.

3.2 FT-IR analyses

The FT-IR spectra of AL, EL, AEL, and IAEL are showed in Fig.2. The typical lignin signals can be seen at 1600, 1510 and 1420 cm^{-1} in all the samples. The intensities of the signals corresponding to methyl and methylene groups (at 2957, 2873 and 1460 cm^{-1}) in EL, AEL and IAEL are higher than those in AL. This suggests that, upon reaction, the skeleton of ECH was successfully added to lignin. The appearance of two new peaks at 910 cm^{-1} and 740 cm^{-1} in the FT-IR spectrum of EL^[29] further validates this hypothesis. Compared to

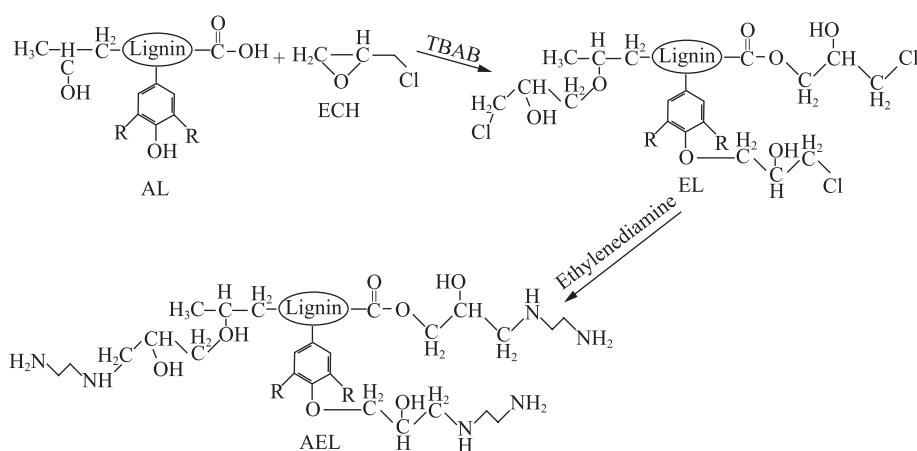


Fig.1 Synthesis route of AEL

the AL spectrum, the more intense peaks at 1120 cm^{-1} and 1030 cm^{-1} in EL, AEL, and IAEL spectra, which correspond to C—N and C—O vibrations, indicate a successful connection between lignin epichlorohydrin and ethylenediamine. In addition, the disappearance of the absorptions at 910 cm^{-1} and 740 cm^{-1} from the AEL and IAEL spectra further demonstrated that the ethylenediamine fragment was incorporated into EL.

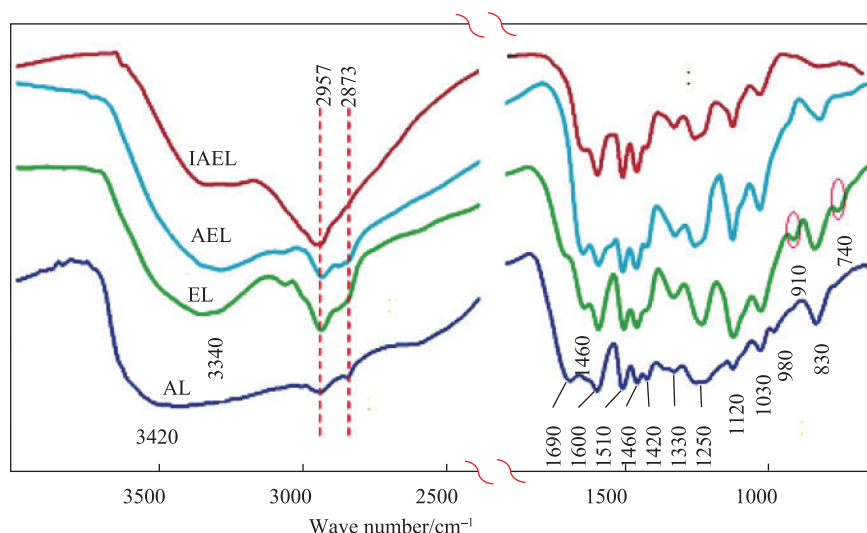
3.3 ^{13}C NMR spectra analysis

The ^{13}C NMR spectra of AL, EL, and AEL are shown in Fig.3. The signal of the methoxy group at $55.7\sim 56.0\text{ ppm}$ is present in all samples, indicating that the methoxy group in lignin is chemically inert during the course of the reaction. The signals of methylene carbons (around $59.7\sim 71.7\text{ ppm}$) can be seen intensified in EL and AEL^[15]. The peak at $52.2\sim 52.6\text{ ppm}$ in EL was corresponded to the methylene group bonded to chlorine^[30] and the peaks at 44.2 and 54.2 ppm associated to the C—N bond^[31-32] were found in the AEL spectrum after amination, indicating the successful amination of lignin. It can be concluded that AEL can be prepared by etherification of lignin with ECH followed by amination with ethylenediamine.

3.4 Evaluation of foamability and emulsification

The foamability of AEL and IAEL at different concentrations is shown in Fig.4 and Table 1. As can be seen, the solution does not bubble when the concentrations of AEL and IAEL in the samples are lower than 0.1% and 0.5% , respectively. However, both of them displayed

good foamability. AEL solution manifested a good foamability, and at concentrations higher than 0.5% , the foam formed in AEL solution remained constant. In the case of IAEL, the foam increases with the increase in its concentration but with lower foam volume of V_1 and V_2 and basically higher ratio of V_1/V_2 then that of AEL, suggesting a decrease in the foamability of AEL after being ionized with HCl.



Note: AL, EL, AEL, and IAEL stand for the starting lignin, etherified lignin, aminated lignin, and ionized aminated lignin, respectively.

Fig.2 FT-IR spectra of AL and modified lignin samples

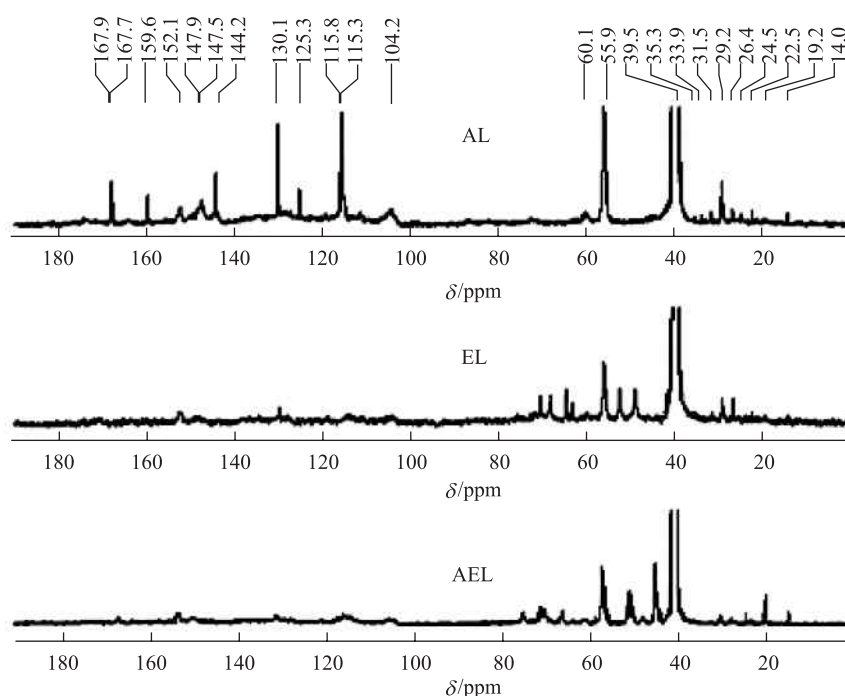
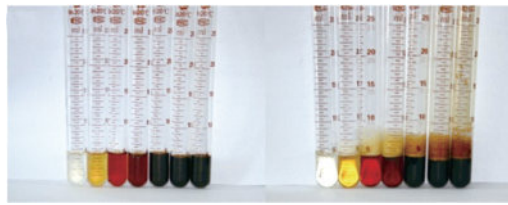
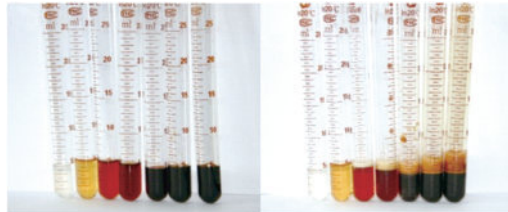


Fig.3 ^{13}C NMR spectra of AL and modified lignin samples



(a) AEL



(b) IAEL

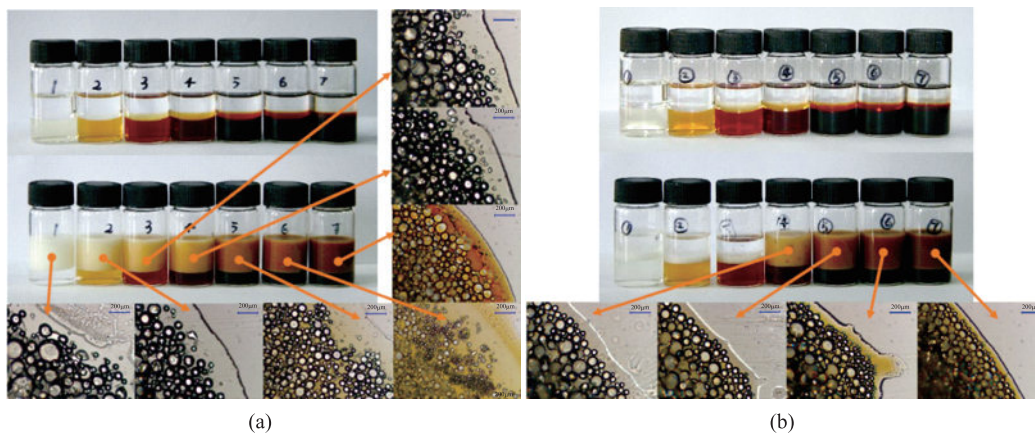
Note: the concentrations of the solutions are 0.01%, 0.1%, 0.5%, 1%, 3%, 5%, and 10%, respectively (from left to right).

Fig.4 Foaming experimental of modified lignin samples in solution

Table 1 Foam volume of sample solution

Samples	Concentration/%	V_1 /mL	V_2 /mL	V_1/V_2
AEL	0.01	1.0	0	—
	0.1	2.5	2.0	1.3
	0.5	5.5	4.0	1.4
	1	4.0	4.0	1.0
	3	4.0	3.0	1.3
	5	3.9	3.5	1.1
	10	4.0	4.0	1.0
IAEL	0.01	0	0	—
	0.1	0	0	—
	0.5	1.0	0.75	1.3
	1	2.5	1.3	1.9
	3	1.5	1.5	1.0
	5	2.4	1.7	1.4
	10	3.2	2.4	1.3

To determine emulsion formation, the modified lignin surfactants were dissolved in deionized water at different concentrations. The emulsions were formed by adding equal volume of *n*-hexanes followed by mixing with a vortex mixer. The images of the emulsification test of AEL and IAEL samples are shown in Fig.5, and the volume and particle size of the emulsion layer formed by AEL and IAEL solutions are reported in Table 2. Two weeks after emulsion formation, we collected microscopic images of the emulsion droplets and measured the emulsion volume fraction. As shown in Table 2, with the increase of AEL concentration in the solution, there is a decrease in the extreme value of the emulsion droplet size. On the contrary, the size of the emulsion droplets in the case of IAEL varies slightly when the IAEL concentration is increased. It can also be seen that, in both AEL and IAEL solutions, more small-sized droplets are formed in the emulsion layer at higher concentrations. Compared with IAEL, the emulsion layer of AEL solution is more stable even at the lowest concentration (0.01%), and it remains almost unchanged even after 3 months when sealed at room temperature. In the low concentration regime (0.01%~0.5%), the demulsification of the IAEL emulsion layer was observed shortly after the emulsifying treatment of the samples, implying that an unstable emulsion layer of *n*-hexane and water was formed. The volume fractions of the emulsion layer are above 70% in the AEL solutions, and show higher values than those of IAEL solutions having the same



Note: the concentrations of the solutions are 0.01%, 0.1%, 0.5%, 1%, 3%, 5%, and 10% (from left to right).

Fig.5 Emulsifying experiments of AEL (a) and IAEL (b) solutions at different concentrations

Table 2 Volume fraction of emulsion, emulsion droplet size, CMC, and surface tension at CMC of modified lignin samples

Samples	Concentration /%	Emulsion volume fraction/%	Emulsion droplet size/ μm	CMC /%	Surface tension at CMC/($\text{mN} \cdot \text{m}^{-1}$)
AEL	0.01	70.56	13~260	1.06	42.98
	0.1	71.35	43~156		
	0.5	71.75	34~156		
	1	71.84	13~147		
	3	71.84	13~113		
	5	71.84	8.7~104		
	10	70.93	8.7~104		
IAEL	0.01	—	—	1.01	36.33
	0.1	—	—		
	0.5	—	—		
	1	62.05	17~139		
	3	68.82	17~139		
	5	70.06	17~139		
	10	70.91	17~113		

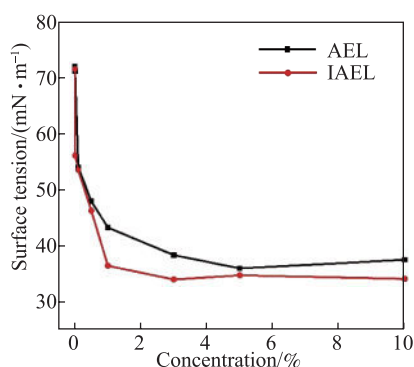


Fig.6 Isotherms of surface tension of water plotted against the concentration of modified lignins

concentration of surfactant, which indicates that the emulsifying ability of AEL decreased after ionization.

3.5 Measurement of surface tension

The surface activity of AEL and IAEL was evaluated based on the ability to reduce the surface tension of aqueous solution at the water-air interface. The critical micelle concentration (CMC) and the corresponding surface tension values for AEL and IAEL samples are shown in Table 2, and the surface tension-concentration isotherms are plotted in Fig.6.

The surface tension of AEL and IAEL solutions displays the same trend. In both cases, the surface tension decreases drastically when the concentration of the lignin-based surfactant in the solution increases.

Above a given concentration threshold, defined as CMC of the surfactant, the surface tension decrease rate becomes slower. Similar CMC values were found for AEL and IAEL (1.06% and 1.01%, respectively). The corresponding surface tension of AEL was 42.89 mN/m at CMC, which was higher than that of IAEL (36.33 mN/m). These results suggest that the surface activity of IAEL is higher than that of AEL. The lignin surfactant prepared in this work showed good surface activity, comparable to that of the ones previously reported for similar surfactants. In Matsushita's

work^[33], the surface tension of aqueous solution of the lignin cationic surfactant derived from phenolation and Mannich reaction with dimethylamine and formaldehyde decreased to 45 mN/m at CMC of 0.4%. Homma et al^[14] prepared non-ionic polymeric surfactants by modifying acetic acid lignin with polyethylene glycol diglycidylethers, and the surface tension of aqueous solution of this lignin derivative was 36 mN/m at CMC of 5%. In our previous work, the surface tension of the solution of other water-soluble lignin derivatives prepared from the reaction of polyethylene glycols (PEG 600 and PEG1000) with epoxy lignin was 43.30 mN/m at CMC of 1.03%. The results of the present study suggest that lignin surfactants with high surface activity can be obtained by modifying lignin with ECH and ethylenediamine.

4 Conclusions

Aminated lignin (AEL) was successfully prepared by the chemical modification of lignin using epichlorohydrin and ethylenediamine. After acidification of AEL, ionized aminated lignin (IAEL) was obtained. Analyses showed that lignin was successfully functionalized and that the nitrogen content of AEL was 6.9%. AEL shows better foamability and emulsifying properties than IAEL.

Surface tension tests suggested that AEL and IAEL had similar critical micelle concentration (CMC). However, IAEL had a smaller surface tension (36.33 mN/m) than AEL (42.89 mN/m) at CMC.

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