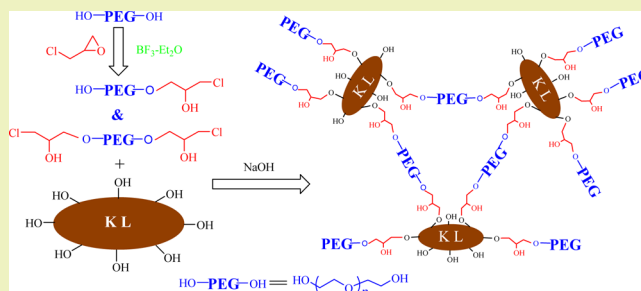


# Synthesis, Structure, and Dispersion Property of a Novel Lignin-Based Polyoxyethylene Ether from Kraft Lignin and Poly(ethylene glycol)

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**ABSTRACT:** In this study, a novel and water-soluble lignin-based polyoxyethylene ether (KL-PEG) was synthesized from kraft lignin (KL) and poly(ethylene glycol) (PEG). PEGs with various polyoxyethylene ether lengths were functionalized preferentially with epichlorohydrin using  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  as the Lewis acid catalyst and then grafted onto KL by blocking the phenolic hydroxyl groups. The generated KL-PEG copolymer was purified successively by extraction, dissolution, and precipitation using butanone, alcohol, and diethyl ether, respectively. The effect of reactant ratios on the structure of the KL-PEG copolymer was investigated by Fourier transform infrared spectra (FTIR), ultraviolet spectrophotometer (UV), gel permeation chromatography (GPC), and functional groups content determination. Solubility and FTIR results revealed the successful introduction of PEG into KL. The PEG content in the KL-PEG copolymer could be controlled by varying the mass ratio of PEG to KL, and the molecular weight could be governed by the molar ratio of epichlorohydrin to PEG. The KL-PEG copolymer was further used as a novel dispersant for 50% dimethomorph suspension concentrates and showed better dispersing and rheological properties comparing with lignosulfonate and PEG. This novel amphiphilic KL-PEG copolymer possessing a renewable lignin backbone and branched PEGs could be a promising dispersant for similar applications, including agricultural suspension concentrates.

**KEYWORDS:** Kraft lignin, Poly(ethylene glycol) (PEG), Epichlorohydrin, Water soluble, Suspension concentrates, Dispersion



## INTRODUCTION

Utilization of biomass resource has drawn increasing attention due to the imminent shortage of fossil fuels. Lignin, an integral part of the cell wall of plants, is the second most abundant and renewable carbon resource on Earth after cellulose.<sup>1</sup> Lignin mainly consists of p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units and has great potential to produce various aromatic compounds or fuel precursors.<sup>2</sup> Technical lignin is produced as a byproduct from the pulping and papermaking industry and cellulosic ethanol industry. Kraft lignin (KL), accounting for nearly 85% of total technical lignin, is typically used as fuel for energy recovery.<sup>1,3</sup> Nevertheless, the application of KL is limited by its poor solubility and reactivity. So far, several attempts have been made to obtain high valuable lignin-based chemicals by means of sulfonation<sup>4–6</sup> and carboxymethylation,<sup>7,8</sup> and the generated products can be used as anionic surfactants in various application areas. A special attempt is the modification of KL with an amphiphilic polymer instead of small hydrophilic functional groups, which would be expected to result in lignin amphiphilic derivatives.

Poly(ethylene glycol) (PEG) is used as one of the most suitable graft-forming polymers because of its unique properties including amphiphilicity, low toxicity, good biocompatibility, and biodegradability.<sup>9</sup> Functionalized PEG is prepared prior to

attaching the PEG to the desired molecule because the terminal hydroxyl groups are much more reactive than the polyoxyethylene chain. PEG derivatives have been proven valuable in a great diversity of chemical and biological endeavors, such as nonionic surfactant, protein conjugates, phase transfer catalysis, aqueous two-phase separation, and pharmaceutical modification.<sup>10</sup>

PEG was modified at one or both terminal hydroxyl groups preferentially in order to graft onto lignin. Recently, some approaches had been developed to modify lignin with PEG derivatives in alkaline solution, typically PEG-mesylate<sup>11</sup> and PEG-epoxide,<sup>12–14</sup> to improve the water solubility of lignin. The modified lignin (lignin-PEG) with PEG derivatives was soluble in methanol, chloroform, and pyridine in addition to water.<sup>12</sup> The lignin-PEG copolymer could improve brightness stabilization and strength properties of high-yield pulps,<sup>11</sup> improve dispersibility and bending strength of cement,<sup>15</sup> and enhance enzymatic hydrolysis of cellulose and lignocelluloses.<sup>16,17</sup> However, the PEG-mesylate was prepared grindingly from PEG methyl ether ( $M_w$  350) by reacting with

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methanesulfonyl chloride in methylene chloride at 0 °C using triethylamine as a catalyst,<sup>11</sup> while the PEG-epoxide was synthesized from PEG by reacting with epichlorohydrin in the presence of BF<sub>3</sub> and then closed loop and dehydrochlorinated in the alkali solution.<sup>18</sup> Monoepoxide PEG derivatives<sup>13</sup> and commercial dodecyloxy-PEG-epoxide<sup>14</sup> could improve the surface activity of lignin further than that of diepoxide PEG derivatives. In a word, the functionalized PEG derivatives above either were prepared in organic solvents or unusual commercial products that made lignin modification with PEG derivatives expensive and complex.

The aim of the present study was to modify KL with PEG in a novel and flexible way. PEGs with different molecular weights reacted with ECH using BF<sub>3</sub>-Et<sub>2</sub>O as a catalyst to produce the PEG-chlorohydrin intermediate. Then, the water-soluble copolymer of KL and PEG (KL-PEG) was synthesized by coupling KL and the PEG-chlorohydrin intermediate. The structure of the KL-PEG copolymer was studied by Fourier transform infrared spectra (FTIR), ultraviolet spectrophotometer (UV), gel permeation chromatography (GPC), and functional groups content determination. The effect of reactant ratio on the structure of the KL-PEG copolymer was investigated. The KL-PEG copolymer, possessing a lignin backbone and branched PEGs, was further used as a novel dispersant for 50% dimethomorph suspension concentrates (SC).

## ■ EXPERIMENTAL SECTION

**Materials and Chemicals.** KL was supplied by Jilin Paper Co., Ltd. in Jilin province, China, which was separated from pinewood kraft pulping liquor using acid precipitation. The lignin purification process was as follows. The lignin was dissolved in alkali solution first and then the impurity was separated from lignin solution by centrifugation. After that, the lignin solution was adjusted to pH 2.0 with hydrochloric acid and the precipitated lignin was filtered on a Buchner funnel and washed with water to remove sugars and inorganic salts. Finally, purified lignin was obtained by drying in an oven at 60 °C under vacuum for 48 h.

Dimethomorph, named (E,Z)-4-[3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl) acryloyl] morpholine, is a systemic fungicide which protects vegetables and plants from downy mildews, late blights, crown, and root rots.<sup>19</sup> Dimethomorph was provided as a light white powder (50 μm) with a minimum purity of 98.5% from Noposion Agrochemicals Co., Ltd., China.

PEG was purchased from Guangdong Guanghua Chemical Factory Co., Ltd. (China). BF<sub>3</sub>-Et<sub>2</sub>O was 47% BF<sub>3</sub> and 53% Et<sub>2</sub>O. Commercial lignosulfonate was byproduct of softwood sulfite pulping from Russia. All chemicals and solvents were of analytical grade and used as received. Milli-Q water was used for the preparation of all solutions.

**Synthesis of KL-PEG Copolymer.** A total of 100 g of PEG was put in a reactor flask equipped with a temperature-controlling electric heating device, motor stirrer, thermometer, peristaltic pump, and reflux condenser. When the solid PEG melted completely under mechanical stirring at 55 °C, 0.8 g of BF<sub>3</sub>-Et<sub>2</sub>O was added into the flask. Subsequently, ECH was added dropwise at a rate that was sufficient to maintain the reaction temperature at 55–60 °C. After dripping off, the reaction was carried on for two more hours at 55 °C. Then the excess ECH was removed by distillation, and the PEG-chlorohydrin intermediate was generated, which the yield was about 80%. KL was dissolved in 1 M sodium hydroxide to prepare a 25% (w/w) lignin solution in another reactor flask. The PEG-chlorohydrin intermediate was dropped into the lignin solution and reacted at 80 °C for 3 h. After cooling, the pH of the solution was adjusted to pH 7 with hydrochloric acid, and water-soluble KL-PEG copolymer was obtained. PEGs with different molecular weights, 600, 1000, and 2000 g mol<sup>-1</sup>, were grafted onto lignin by the above procedure. The molar ratio of ECH to PEG varied with *M<sub>w</sub>* of PEG and performed in

an appropriate range to avoid excessive cross-linking of KL by the PEG-dichlorohydrin intermediate.

**Purification of KL-PEG Copolymer.** First, the product was extracted successively with butanone to remove unreacted PEG and water until a sticky granule appeared and then was dissolving in ethanol for 1 h. Afterward, insoluble lignin was isolated by centrifuging at 10,000 rpm for 10 min (Sigma 3–15, Germany), and the supernatant was concentrated by vacuum rotary evaporation. After that, a concentrated ethanol solution of KL-PEG copolymer was precipitated by adding diethyl ether, and finally, the precipitate was dried in-vacuo at 50 °C to get the purified KL-PEG copolymer.

**Solubility Property.** Various test solutions of a KL-PEG copolymer, physical mixture of PEG+KL, and KL control, of which the lignin and PEG concentration was kept at 100 and 133 mg L<sup>-1</sup> separately, were prepared. The solution pH was adjusted to the desired level with 0.1 M sodium hydroxide and 0.1 M hydrochloric acid, and then, the suspension was centrifuged at 10,000 rpm for 10 min by using a high-speed centrifuge (Sigma, model 1-14, Germany). The absorbance at 276.5 nm of supernatant was measured for each test solution at room temperature (UV-2550, Shimadzu Corp., Japan).

**FTIR Analysis.** The FTIR spectra of different samples pressed with KBr at a ratio of 1/100 were collected by a Vector 33 spectrometer (Bruker Corp., Germany). The region between 400 and 4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> and 32 scans was recorded. The FTIR spectrometer was calibrated for background signal scanning with air first, and then, the experimental sample scanning was conducted.

**PEG Content Determination.** The PEG content in the KL-PEG copolymer was measured indirectly through the UV spectrophotometric method. The absorbance at 276.5 nm of the PEG-g-KL polymer solution was contributed by KL because the PEG aqueous solution showed no absorbance near 280 nm. The KL calibration curve was  $Y = 0.0244X - 0.0001$ ,  $R^2 = 0.9999$ , ( $Y$  = absorbance,  $X$  = concentration, mg L<sup>-1</sup>) that was calculated from the absorbance at 276.5 nm of a series of KL solutions with pH 7.5 from 10 to 100 mg L<sup>-1</sup>. A known concentration of KL-PEG copolymer solution with pH 7.5 was prepared to measure the lignin content using the calibration curve; thus, PEG content was obtained. Analyses were performed thrice for each sample, and mean values were reported.

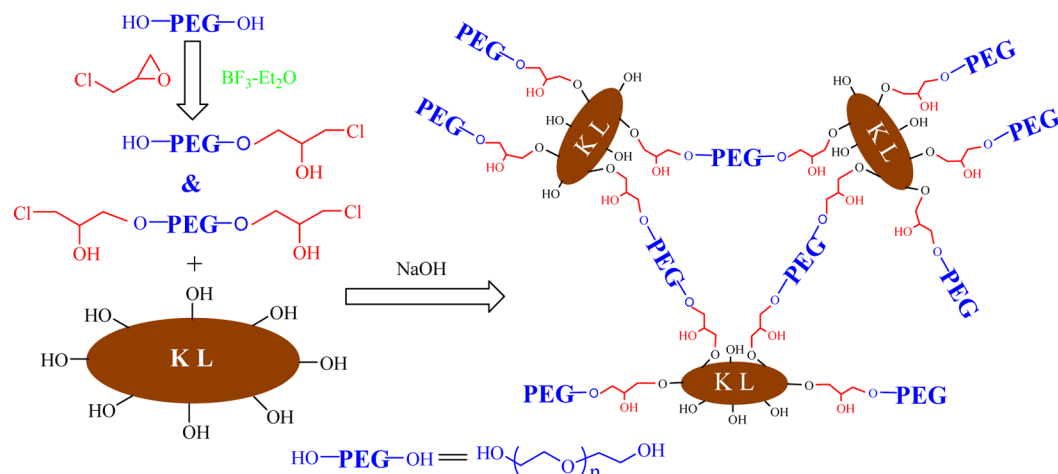
**Phenolic Hydroxyl Group (Ph–OH) Content Determination.** Ph–OH contents of KL and KL-PEG copolymers were determined by the Folin–Ciocalteu colorimetric method with vanillin as the reference substance. The detailed procedure was described in our previous study.<sup>20</sup> Chromogenic reaction time was 2 h, and the absorbance of the solution was measured immediately at 760 nm. The Ph–OH content was determined by the calibration curve of vanillin standard. Analyses were performed in triplicate for each sample. Mean values were reported, and the experimental errors were less than 0.01 mmol g<sup>-1</sup>.

**Molecular Weight Distribution.** The molecular weight distribution of KL and KL-PEG copolymers was determined by GPC with Ultrahragel120 and Ultrahragel250 columns. The 0.10 M NaNO<sub>3</sub> aqueous solution with pH 10 was used as the mobile phase at a flow rate of 0.5 mL min<sup>-1</sup>.<sup>21</sup> The effluent was monitored at 280 nm with a Waters 2487UV absorbance detector (Waters Corp., U.S.A.). Sodium polystyrenesulfonate standards from 2000 to 100,000 g mol<sup>-1</sup> were used for calibration. All samples were dissolved by the GPC mobile phase and filtrated by 0.22 μm syringe filter.

**Preparation of Dimethomorph SC.** Fifty percent (w/w) dimethomorph SC were prepared by wet milling with a planetary ball mill (QM-3SP2, Nanjing University Instrument Factory, China). Dimethomorph (50 g), dispersant (2.5 g), and Milli-Q water (47.5 g) were mixed and added to a grinding jar filled with zirconium balls (300 g) with a diameter of 10 mm. The rotation rate was set at 400r/min and ran for 2 h to target particle size <5 μm, and then dimethomorph SC was obtained.

**Dispersibility Measurement of Dimethomorph SC.** The particle size distribution of dimethomorph SC was analyzed by means of MS2000 laser diffraction particle size analyzer equipped with Hydro SM wet dispersion unit (Malvern Instruments, U.K.). The

Scheme 1. Synthesis Mechanism of KL-PEG Copolymer



dispersion medium was Milli-Q water, and the volume-based mean diameter was reported as the average particle size.

Suspensibility tests on the SC were performed according to Collaborative International Pesticides Analytical Council (CIPAC) Method MT161. The remaining tenth of the suspension was assayed gravimetrically after dried, and the total suspensibility was calculated. Analyses were performed in duplicate for each sample.

**Rheological Measurement of Dimethomorph SC.** The rheological properties of dimethomorph SC were conducted with HAAKE MARS III rotational rheometer (Thermo Fisher Scientific, U.S.A.) equipped with a cylindrical rotor of CC26Ti at  $25.0 \pm 0.1$  °C. Each sample rested for 5 min before measurement to eliminate the effect of pouring and attain the temperature equilibrium. Rheological measurement was carried out according to the following procedure: shear rate from  $0.0001$  to  $1 \text{ s}^{-1}$  in CS mode for 10 s, then linearly increased to  $200 \text{ s}^{-1}$  in CR mode for 120 s, and finally reduced to  $0.0001 \text{ s}^{-1}$  in a further period of 120 s. Shear stress and shear viscosity were monitored, and the viscosity at shear rate of  $100 \text{ s}^{-1}$  was used as the apparent viscosity of dimethomorph SC. Each sample was measured at least twice.

## RESULTS AND DISCUSSION

**Synthesis of KL-PEG Copolymer.** To react with Ph-OH in KL, PEG should be modified preferentially to provide reactive functional sites. First, protonation of ECH produced an oxonium ion in the presence of  $\text{BF}_3\text{-Et}_2\text{O}$  as the Lewis acid catalyst and reacted with terminal hydroxyl groups of PEG.<sup>22,23</sup> Because PEG contained hydroxyl on both ends, at least one of the hydroxyl groups would react to form the chlorohydrin ether group. Thus, the generated PEG-chlorohydrin intermediate was monochlorohydrin ether or dichlorohydrin ether, as well as mixtures of both as shown in Scheme 1, that was governed by the molar ratio of ECH to PEG taken during the reaction.

Free Ph-OH in KL was blocked by etherification with the PEG-chlorohydrin intermediate under alkaline condition. Ph-OH in KL was ionized with  $\text{pH} > 12.6$  to form phenoxide ions, which were strong nucleophile.<sup>11,24</sup> The synthesis mechanism of the KL-PEG copolymer are illustrated in Scheme 1. The monochlorohydrin intermediate was attached to KL to improve hydrophilicity, and the dichlorohydrin intermediate played as cross-linker to produce a high polymer, which had a relation with the feeding molar ratio of ECH to PEG. A sodium hydroxide solution herein acted as the solvent of KL as well as the acid scavenger to bind the generating hydrochloric acid.

**Purification of KL-PEG Copolymer.** Ultrafiltration was useful to separate low molecular weight reagents and impurities

from PEG derivatives when the derivative preparation was conducted in water. However, the strong hydrophilicity of PEG and hydrogen bonding<sup>25</sup> interactions between PEG and KL meant the separation of unreacted PEG cannot be accomplished completely by ultrafiltration. Therefore, the purification process of the KL-PEG copolymer was executed by taking advantage of the solubility properties of PEG, KL, and copolymer.

First, a solvent could extract both PEG and water, but instead of the KL-PEG copolymer was required. PEG was soluble in alcohols, ketones, chloroform, glycerides, arenes, and so on, while the KL-PEG copolymer had good solubilities in alcohols, chloroform, DMSO, and DMF. Therefore, ketones were taken into consideration. Acetone was miscible with water easily and could extract a part of the KL-PEG copolymer as well as PEG and water, so butanone satisfied both and was selected. Unreacted PEG, sodium chloride, and water were removed after successive extraction by butanone. Second, the precipitate was dissolved in ethanol, and then, undissolved KL (10%) and KL-PEG with a low grafting degree (20%) was separated by centrifuging. The supernatant was the desired product PEG-KL with a high grafting degree, of which was about 60% based on the amount of originally feeding KL and PEG.

**Solubility.** To verify whether PEG and KL were covalent cross-linked or just physical interactions, the absorbance at 276.5 nm as a function of pH for the KL-PEG copolymer, KL + PEG mixture, and KL control aqueous solutions were investigated (Figure 1). The absorbance at 276.5 nm represented the lignin solubility in aqueous solution. Results showed that KL+PEG mixture behaved similarly to KL control solutions. The absorbance remarkably decreased and flocculate sedimented at pH 2.0, which was expected for lignin. In contrast, the absorbance of KL-PEG copolymer solutions with various PEG chain lengths decreased slightly, and the solutions remained clear with decreasing pH. The KL-PEG copolymer solution with 10% (w/w) concentration was absolutely soluble even though the pH was adjusted to 1.0, indicating KL-PEG copolymer had a good solubility in water at a wide pH range. Thus, the covalent attachment of amphiphilic polyoxyethylene ether greatly improved the hydrophilic performance of KL.

**FTIR Analysis.** A comparison of the FTIR spectra of KL with the PEG-modified counterpart KL-PEG1000 clearly revealed differences in the frequency range and fingerprint



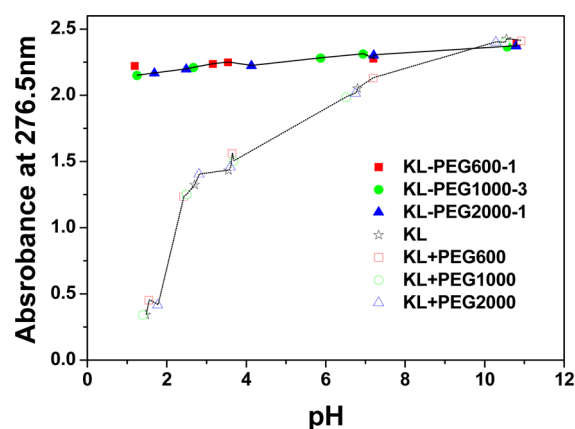


Figure 1. Absorbance at 276.5 nm as a function of pH of the KL-PEG copolymer, KL+PEG mixture, and KL aqueous solutions.

region (Figure 2a), which was the result of the introduction of polyoxyethylene ether to KL.

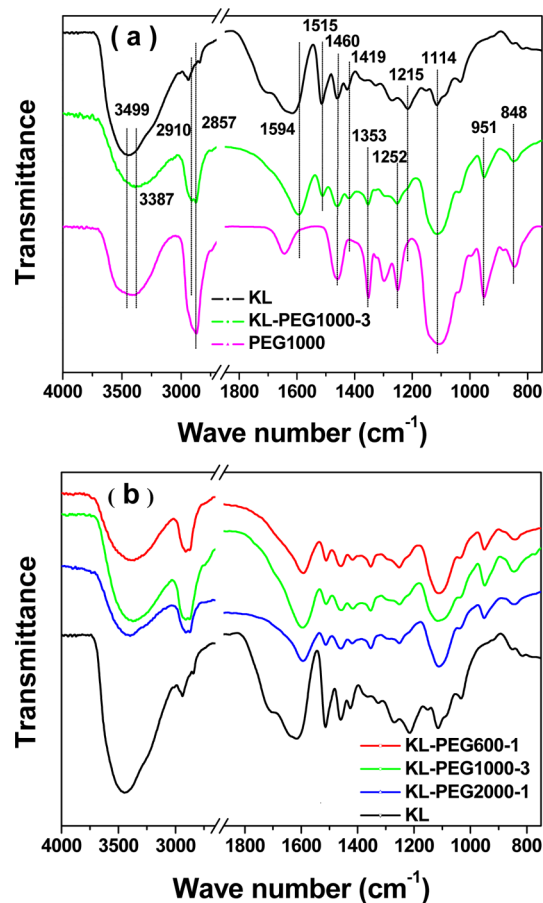


Figure 2. (a) FTIR spectra of KL, PEG1000, and KL-PEG1000-3. (b) FTIR spectra of KL, KL-PEG600, KL-PEG1000, and KL-PEG2000.

The unmodified KL showed typical and intense signals that were assigned to hydroxyl group stretching vibration ( $3499\text{ cm}^{-1}$ ), C–H stretching of methyl, methylene, or methoxy groups ( $2939\text{ cm}^{-1}$ ), aromatic ring skeleton vibrations ( $1617$ ,  $1515$ , and  $1426\text{ cm}^{-1}$ ), and C–H in-plane bending vibrations of methyl and methylene.<sup>1,26,27</sup> Signals at  $1216$  and  $1115\text{ cm}^{-1}$  were related to aromatic C–O stretching and aromatic C–H in-plane deformation, respectively.<sup>28,29</sup>

The appearance of very intense bands of the PEGylated KL at  $1114$  and  $951\text{ cm}^{-1}$ , which were attributed to the C–O–C stretching vibration, clearly indicated the successful introduction of polyoxyethylene ether.<sup>30</sup> This was also supported by the increased intensity of the bands at  $2910$  and  $2857\text{ cm}^{-1}$ , which originated from the C–H stretching of methyl and methylene in PEG. Furthermore, the emerging bands at  $1353$  and  $848\text{ cm}^{-1}$  corresponding to the C–H bending vibration and  $1252\text{ cm}^{-1}$  corresponding to the C–C stretching vibration were also observed due to the graft reaction of the PEG intermediate onto lignin macromolecular. The hydroxyl group stretching vibration showed a broader band at the lower wavenumber compared to that of the unmodified KL, which accounted for the formation of secondary aliphatic hydroxyl groups<sup>29</sup> according with Scheme 1. The intensity of the band at  $1216\text{ cm}^{-1}$  became less apparent, which was consistent with the determination of the Ph–OH content, indicating that the Ph–OH of KL was etherified by the PEG-chlorohydrin intermediate.<sup>30</sup>

The FTIR spectra of KL-PEG600 and KL-PEG2000 polymers showed very similar changes with that of KL-PEG1000 (Figure 2b). FTIR analysis indicated PEG had been successfully grafted into KL.

FTIR spectroscopy had been used to quantitatively determine the lignin content in wood using the peak at  $1505\text{ cm}^{-1}$  as reference,<sup>31</sup> which assigned to the aromatic ring skeleton vibration. Therefore, the  $1515\text{ cm}^{-1}$  peak was regarded as the reference peak.<sup>32</sup> The absorbance ratios of the characteristic peaks and reference peak were calculated (Table 1) to analyze the structural changes of modified KL.<sup>33</sup> With the increase in weight ratio of PEG to KL,  $A_{1114}/A_{1515}$ ,  $A_{1252}/A_{1515}$ ,  $A_{1352}/A_{1515}$ , and  $A_{2857}/A_{1515}$  increased as well, indicating more PEG chains had been introduced into KL.

**Structural Characterization.** The UV spectrum of the KL-PEG copolymer solution was similar to that of the KL solution (data did not show), and the characteristic absorption peak had a blue shift from  $276.5$  to  $274.5\text{ nm}$  due to the etherification of the Ph–OH groups. The Ph–OH content in the KL-PEG copolymer was attributed to lignin and was converted to lignin-based in order to analyze the change in Ph–OH content. The ratio of the Ph–OH content decrement to that of the original KL ( $2.73\text{ mmol g}^{-1}$ ) was defined as a substitution degree (SD) of Ph–OH.

The weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ), and polydispersity ( $M_w/M_n^{-1}$ ) of KL and KL-PEG copolymers are presented in Table 2. The

Table 1. Absorbance Ratios of Characteristic Peaks and Reference Peak of KL and KL-PEG1000 Copolymers

wavenumber	KL	KL-PEG1000-2	KL-PEG1000-3	KL-PEG1000-4
$A_{1114}/A_{1515}$	1.0308	1.6748	1.9168	3.6346
$A_{1252}/A_{1515}$	0.9003	1.0749	1.1422	1.4423
$A_{1352}/A_{1515}$	0.6064	1.0897	1.1587	1.4892
$A_{2857}/A_{1515}$	0.3820	0.9118	1.1181	1.7731

**Table 2.** Weight-Average Molecular Weight ( $M_w$ ), Number-Average Molecular Weight ( $M_n$ ), and  $M_w \cdot M_n^{-1}$  of KL and KL-PEG Polymers

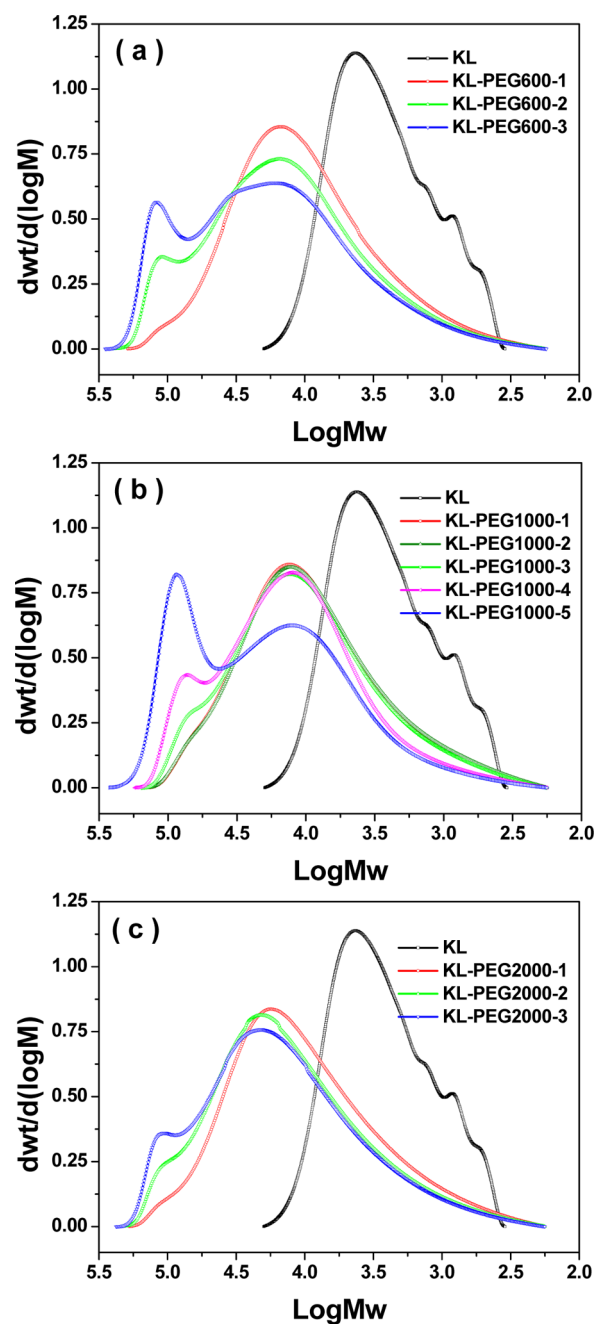
sample	ECH/PEG molar ratio	PEG/KL mass ratio	$M_w$	$M_n$	$M_w \cdot M_n^{-1}$
KL	—	—	3610	1925	1.87
KL-PEG600-1	0.5	1.33	18 061	4761	3.79
KL-PEG600-2	0.75	1.33	28 286	5690	4.97
KL-PEG600-3	1	1.33	37 031	6320	5.86
KL-PEG1000-1	0.5	1.33	15 928	4179	3.81
KL-PEG1000-2	0.75	1	15 843	4033	3.93
KL-PEG1000-3	0.75	1.33	18 152	4372	4.15
KL-PEG1000-4	0.75	2	23 069	5748	4.01
KL-PEG1000-5	1	1.33	36 618	6899	5.31
KL-PEG2000-1	1	1.33	18 733	4445	4.21
KL-PEG2000-2	1.25	1.33	25 008	5379	4.65
KL-PEG2000-3	1.5	1.33	29 201	5772	5.06

molecular weight distributions of KL and KL-PEG polymers are shown in Figure 3. KL-PEG copolymers had a much larger  $M_w$  and  $M_w \cdot M_n^{-1}$  than the original KL. The average molar number of PEG chains and KL in the copolymer, which meant the degree of grafting and cross-linking, respectively, was calculated by the PEG content and the  $M_w$  of KL and KL-PEG polymers.

**Effect of Molar Ratio of ECH to PEG on the Composition of KL-PEG Copolymer.** ECH acted as a reagent to bridging KL and PEG and had an important effect on the composition of the KL-PEG copolymer. Comparing the composition of KL-PEG600 copolymers, with the increase in molar ratio of ECH to PEG, the  $M_w$  of KL-PEG copolymers significantly increased from 18,061 to 37,031 g mol<sup>-1</sup> and polydispersity from 3.79 to 5.86, respectively. The average molar number of KL in the KL-PEG600 copolymers increased from 2.37 to 4.26 mol/mol copolymer (Table 3), which was in accordance with the molecular weight distributions of KL-PEG600 copolymers (Figure 3a). Results showed that more PEG-dichlorohydrin intermediates formed and cross-linked KL to produce a high polymer, of which log  $M_w$  was about 5.1, as a result of the increase in molar ratio of ECH to PEG. The SD of Ph-OH increased from 50.0% to 65.7%, with the increase in ECH, which indicated Ph-OH in KL was blocked with the PEG-chlorohydrin intermediate. KL-PEG copolymers with PEG1000 and PEG2000 presented the same trend as that of the KL-PEG600 copolymers (Figure 3b,c).

The  $M_w$  of KL-PEG copolymers could be regulated through varying the molar ratio of ECH to PEG but showed a high polydispersity. When the molar ratio of ECH to PEG exceeded an appropriate value, the water-soluble KL-PEG copolymer changed to form a hydrogel. It was suggested that the PEG-dichlorohydrin intermediate was dominant and acted as a cross-linker like poly(ethylene glycol) diglycidyl ether to produce a three-dimensional network structural lignin hydrogel.<sup>34</sup>

**Effect of Mass Ratio of PEG to KL on the Composition of KL-PEG Copolymer.** Comparing the composition of the KL-PEG1000 copolymers, of which the molar ratio of ECH to PEG1000 was kept at 0.75 with the increase in mass ratio of PEG to KL, the PEG content increased from 56.62% to 64.23%, which was in conformity with the FTIR results. The  $M_w$  of the KL-PEG copolymers increased from 15,843 to 23,069 g mol<sup>-1</sup>, and the polydispersity changed slightly. The average molar number of PEG increased from 4.71 to 6.18 mol/mol KL, and the average molar number of KL had a slight

**Figure 3.** Molecular weight distributions of KL and KL-PEG copolymers: (a) KL-PEG600 copolymers, (b) KL-PEG1000 copolymers, (c) KL-PEG2000 copolymers.

increase as the PEG/KL ratio increased (Table 3). Results indicated that more polyoxyethylene ether was attached to KL with the increase in mass ratio of PEG to KL; thus, the PEG content and  $M_w$  of the KL-PEG copolymer increased as well. The SD of Ph-OH increased as expected with the increasing demand of Ph-OH to react with the PEG-chlorohydrin intermediate.

The PEG content of KL-PEG copolymers showed from 52.57% to 59.47% varying from the reaction condition and could be controlled by the mass ratio of PEG to KL. However, the mass ratio of PEG to KL was more than one to ensure enough polyoxyethylene ether to improve the hydrophilicity of KL.

Table 3. Structural Compositions of KL-PEG Copolymers

sample	PEG content (wt %)	SD (%)	PEG (mol/mol KL)	KL (mol/mol KL-PEG)
KL-PEG600-1	52.57	50.0	6.67	2.37
KL-PEG600-2	56.71	61.6	7.88	3.39
KL-PEG600-3	58.44	65.7	8.46	4.26
KL-PEG1000-1	61.71	42.6	5.82	1.69
KL-PEG1000-2	56.62	40.5	4.71	1.90
KL-PEG1000-3	59.02	47.4	5.20	2.06
KL-PEG1000-4	64.23	52.9	6.48	2.29
KL-PEG1000-5	62.89	58.6	6.12	3.76
KL-PEG2000-1	57.52	37.6	2.44	2.20
KL-PEG2000-2	57.06	39.6	2.40	2.97
KL-PEG2000-3	59.47	45.2	2.65	3.28

**Effect of PEG Chain Length on the Composition of KL-PEG Copolymer.** We compared the composition of KL-PEG600-1, KL-PEG1000-3, and KL-PEG2000-1, of which the mass ratio of PEG to KL was set at 1.33, to analyze the effect of the PEG chain length on the composition of the KL-PEG copolymer. The  $M_w$  of three KL-PEG copolymers was about  $18,000 \text{ g mol}^{-1}$ , and the average molar number of KL was 2 mol/mol copolymer. The SD of Ph-OH was 50.0%, 47.4%, and 37.6%, respectively, and the average molar number of PEG was 6.67, 5.20, and 2.44 mol/mol KL, respectively, with an increase in PEG chain length from PEG600 to PEG2000. These were because the molar ratio of PEG to KL decreased as the  $M_w$  of PEG increased, and the SD of Ph-OH and the average molar number of PEG in the copolymer decreased.

When PEG400 was used to modify KL, the hydrophilicity of the KL derivative was inferior to the KL-PEG copolymers discussed above. The reason was that the free Ph-OH of the KL was not sufficient, and the PEG chain was too short to provide enough hydrophilicity. But, when PEG4000 was employed, KL could be converted to a hydrophile by increasing the PEG amount, and that was as a result of the low activity of the end hydroxyl groups of PEG4000.

**Dispersion Property of Dimethomorph SC.** The main dosage forms of dimethomorph are wettable powders, water dispersible granules, and suspension concentrates. When dimethomorph was applied, the low concentration suspension was unstable due to the agglomeration, Ostwald ripening, and sedimentation of particles, but it would be dispersed well with the addition of lignosulfonate, which adsorbs on the particle surface and weakens the aggregation of particles through the electrostatic repulsive forces.<sup>35,36</sup> When preparing 50% dimethomorph SC with 2.5% dispersant, it was found that dimethomorph SC prepared with lignosulfonate and KL-PEG was capable of flowing, but dimethomorph SC prepared with no dispersant, PEG600, PEG1000, or PEG2000 caked and cannot flow. The possible cause of this phenomenon was that lignin derivatives adsorbed on the particle to improve its wettability and dispersibility, while PEG had good solubility and did not adsorb on the particle. The average particle size of dimethomorph SC prepared with lignosulfonate and KL-PEG was about  $2.4 \mu\text{m}$  (Table 4). The suspensibility of dimethomorph SC prepared with KL-PEG copolymer, which was 98.6%, 97.8%, and 99.2% corresponding to KL-PEG600-1, KL-PEG1000-3, and KL-PEG2000-1, respectively, was more than that of lignosulfonate, which was 93.1%, indicating the KL-PEG showed better dispersion performance for dimethomorph SC than lignosulfonate.

Table 4. Dispersion Properties of 50% Dimethomorph SC with Different Dispersants

dispersant	partical size ( $\mu\text{m}$ )	suspensibility (%)	apparent viscosity ( $\text{mPa s}$ )
lignosulfonate	2.46	$93.1 \pm 1.5$	177
KL-PEG600-1	2.18	$98.6 \pm 0.9$	66
KL-PEG1000-3	2.41	$97.8 \pm 1.3$	78
KL-PEG2000-1	2.43	$99.2 \pm 1.1$	55

**Rheological Behavior of Dimethomorph SC.** The rheological properties of dimethomorph SC were related to its application and storage. The viscosity curve and flow curve of dimethomorph SC prepared with the KL-PEG copolymer are presented in Figure 4. The shear viscosity of dimethomorph

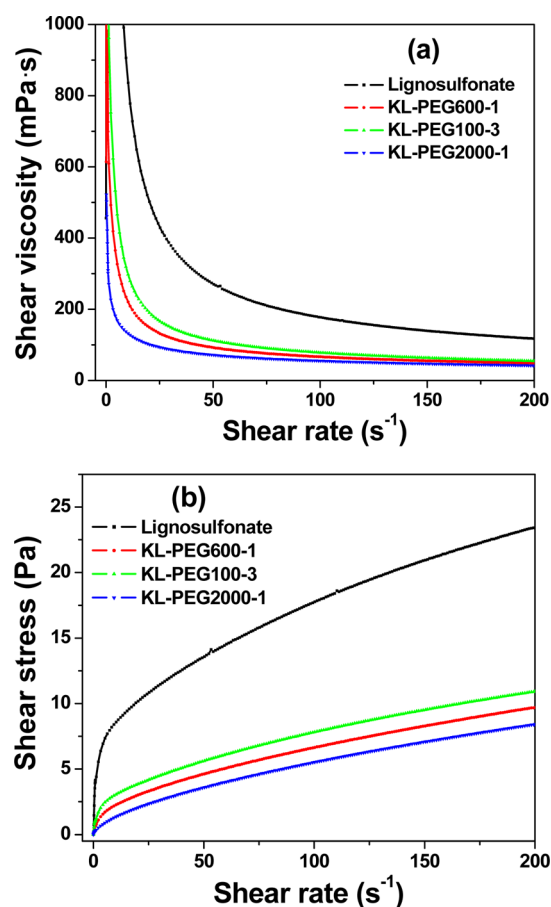


Figure 4. Shear viscosity curve (a) and flow curve (b) of 50% dimethomorph SC prepared with 2.5% KL-PEG copolymer and lignosulfonate.

SC decreased with the increase in shear rate until a steady state was approached in Figure 4a, which showed a typical shear thinning behavior. The apparent viscosity of dimethomorph SC prepared with the KL-PEG copolymer was less obviously than that with lignosulfonate. In Figure 4b, it is shown that the flow curve has pseudoplastic behavior with a yield stress. The Herschel–Bulkley model, which obeys eq 1, where  $\tau_0$ ,  $K$ , and  $n$  denote the yield stress, fluid consistency coefficient, and flow characteristic exponential, respectively, was commonly used to describe the flow curve of pseudoplastic.<sup>37,38</sup> The flow curves of dimethomorph SC were fitted well by the Herschel–Bulkley model, and the correlation coefficient  $R^2$  was more than 0.99



(Table 5). With the decrease in the apparent viscosities of dimethomorph SC prepared with different dispersants, the flow

**Table 5. Fitting Parameters for Herschel–Bulkley Model of 50% Dimethomorph SC with Different Dispersants**

dispersant	$\tau_0$ (Pa)	$K$ (Pa $S^n$ )	$n$	$R^2$
lignosulfonate	1.067	2.676	0.399	0.9981
KL-PEG600-1	0.565	0.415	0.583	0.9999
KL-PEG1000-3	0.303	0.802	0.487	0.9993
KL-PEG2000-1	-0.021	0.329	0.613	1.0000

characteristic exponential  $n$  increased and the fluid consistency coefficient  $K$  decreased. Dimethomorph SC prepared with the KL-PEG copolymer showed lower yield stress  $\tau_0$  and apparent viscosity than that with lignosulfonate, which suggested the KL-PEG copolymer displayed better rheological performance for dimethomorph SC than lignosulfonate.

In summary, the KL-PEG copolymer was a promising dispersant for agricultural chemical SC. The effects of the PEG chain length, PEG content, and molecular weight of the KL-PEG copolymer on the dispersion and rheological properties of dimethomorph SC were necessary for further investigation.

$$\tau = \tau_0 + K \times D^n \quad (1)$$

## CONCLUSIONS

PEGs with various polyoxyethylene ether lengths were functionalized preferentially with ECH using  $BF_3 \cdot Et_2O$  as the Lewis acid catalyst and then grafted onto kraft lignin by blocking the phenolic hydroxyl groups. The covalent attachment of amphiphilic polyoxyethylene ether greatly improved the hydrophilic performance of KL. The novel synthetic approach made the preparing of different grafting and cross-linking degrees of the KL-PEG copolymer flexible and feasible. The PEG content in the KL-PEG copolymer could be controlled by varying the mass ratio of PEG to KL, and the  $M_w$  could be governed by the molar ratio of ECH to PEG.

Fifty percent dimethomorph suspension concentrates prepared with the KL-PEG copolymer as dispersant showed higher suspensibility and lower apparent viscosity compared with lignosulfonate, indicating KL-PEG had a better dispersing ability for dimethomorph suspension concentrates. This novel amphiphilic KL-PEG copolymer possessing a lignin backbone and branched PEGs could be a promising dispersant for similar applications, including agricultural suspension concentrates.

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### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

KL, kraft lignin; PEG, poly(ethylene glycol); ECH, epichlorohydrin; KL-PEG, copolymer of KL and PEG; FTIR, Fourier transform infrared spectra; UV, ultraviolet visible spectra; GPC, gel permeation chromatography; SC, suspension concentrates; Ph-OH, phenolic hydroxyl group;  $M_w$ , weight-average molecular weight;  $M_n$ , number-average molecular weight; SD, substitution degree

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