Preparation and Properties of Hydrogels Based on PEGylated Lignosulfonate Amine

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ABSTRACT: Sodium lignosulfonate (SLS) was aminated to obtain a lignin amine (LA) compound, which was subsequently crosslinked with poly(ethylene glycol) diglycidyl ether (PEGDGE) to obtain hydrogels. The chemical structure of the resulting LA-derived hydrogel (LAH) was characterized by Fourier transform infrared (FTIR) spectroscopy, solid-state 13C NMR spectroscopy, and elemental analysis, and the interior morphology of the freeze-dried hydrogel was examined by scanning electron microscopy. NMR and FTIR spectroscopy results indicated that the amino groups of LA reacted with PEGDGE in the crosslinking reaction. The lignin content in the resulting hydrogel increased with an increase in the LA/PEGDGE weight ratio in the reaction, approaching a maximum (~71 wt %) and leveling off. The hydrogel with such a composition happened to be the same as the one prepared by reacting the primary amines of LA and epoxy groups of PEGDGE in equal stoichiometry. These results strongly suggest that the formation of the hydrogel network structure was largely dictated by the reactions between the primary amines and epoxy groups. The gels with lignin contents at this level exhibited a superior swelling capacity, viscoelasticity, and shear properties.

INTRODUCTION

Sodium lignosulfonate (SLS) is an inexpensive byproduct obtained from sulfite pulping manufacturing. Because SLS contains many sulfate salt groups, it is a water-soluble polymer. Lignosulfonate has been used as a low-cost surfactant and dispersant in some applications, such as concrete admixtures,1,2 coal slurry in water,3 and dyestuff.4 Owing to its renewable and water-soluble characteristics, in recent years lignosulfonate has also been widely investigated for the preparation of hydrogel products.

Nowadays, the market of hydrogel products is growing rapidly. Depending on their chemical structures and properties, hydrogels are used for many different applications. Most hydrogels are used in hygiene products5 and only a small proportion is used for applications such as contact lenses,10 tissue engineering scaffolds,11 drug-delivery systems,12 and wound dressings.13 Recently, there is a growing interest in using lignin-based aerogels and carbon aerogels for advanced applications, such as energy storage,14 environmental remediation,15 etc. Nonetheless, except for some starch- and protein-based hydrogel products, which have only found certain niche applications,16,17 current commercially available hydrogel products are almost entirely made from petrochemical feedstock, especially from acrylic acid and acrylamide monomers.18 In recent years, hydrogels based on natural polymers, such as cellulose and hemicellulose, have also received considerable attention.19

However, there are only a few reports on lignosulfonate-derived hydrogels in the literature. In those studies, hydrogels based on lignosulfonate or modified lignosulfonate feedstocks are mainly prepared through self-crosslinking or crosslinking with other polymers.20 For example, in one study xanthan and lignosulfonate were crosslinked with epichlorohydrin to form a xanthan–lignosulfonate hydrogel. However, the yield of the hydrogels decreased from 87 to 48% with an increase in the lignosulfonate content from 5 to 40 wt %.21 In another study, the dichromate ion was found to be an efficient crosslinking agent for gel formation and the gels made from solutions with SLS contents varying from 5 to 30 wt % exhibited an elastic modulus ranging from 1 to 40 kPa.6 Although the elastic modulus of the gel was improved by this method, the use of a chromium salt could cause significant environmental pollution. Wu et al. graft-copolymerized magnesium lignosulfonate with acrylic acid and acrylamide using potassium persulfate as an initiator and N,N′-methylene-bis-acrylamide as a crosslinker to obtain a superabsorbent hydrogel.7 The swelling capacity of the...
gel decreased with increasing lignin content in the gel, indicating that the swelling capacity was mainly determined by the acrylic acid and acrylamide contents. In another study, a hydrogel was prepared by the reaction between an oligo-(oxyethylene)-grafted SLS and poly(ethylene glycol) diglycidyl ether (PEGDGE), but the swelling capacity of the obtained gel was only 8.1 g/g.8 So far, lignosulfonate-based hydrogels with a high swelling capacity have only been obtained via graft copolymerization with acrylic acid or acrylamide, and the swelling capacity generally decreases with increasing lignin content in the hydrogel. However, those lignin-based hydrogels from all of the above preparation methods have a low lignin content. Therefore, it is necessary to develop a new method for the synthesis of lignin-based hydrogels with a high lignin content.

In this work, a new lignin-based hydrogel was prepared from lignin amine (LA) and PEGDGE. LA was prepared via the Mannich reaction by reacting SLS with formaldehyde and diethylenetriamine (DETA). In the literature, LA has often been prepared by the Mannich reaction and used as flocculants, precipitants, asphalt emulsifiers, oil well cement additives, and cationic dispersants.21−23 Because amine groups usually have a much higher reactivity than hydroxyl groups in reacting with epoxy groups, the aminated lignin derivatives are expected to react with PEGDGE more effectively than SLS itself, resulting in hydrogel products with higher gel contents. To the best of our knowledge, the use of LA for hydrogel preparation has not been reported elsewhere.

## RESULTS AND DISCUSSION

### Synthesis and Characterizations of LA

According to previous studies in the literature,5,8 the hydroxyl groups in SLS are not reactive enough for a crosslinking reaction to achieve hydrogels with a high lignin content and good swelling capacity. To improve the reactivity, lignosulfonate was modified through the introduction of amino groups into its molecular structure in this study. The Mannich reaction is a frequently used method for introducing alkyl amino groups to the aromatic ring of lignin.24 Scheme 1 gives a schematic illustration of the reaction and the possible structure of the formed LA. In this work, DETA was used as an amination agent, which has two primary amino groups in its structure. The LA structure shown in Scheme 1 is one of many possible structures formed and has the maximum primary amino groups. The resulting LA with a high primary amino content could greatly enhance the efficiency of high hydrogel formation.

![Scheme 1. Schematic Illustration of the Structure of a Possible LA Product Prepared Using the Mannich Reaction](image1)

Figure 1 shows a comparison of Fourier transform infrared (FTIR) spectra between SLS and LA. The spectra display both typical and specific characteristics for each lignin sample.25,26 With the peak of benzene skeleton vibrations, at 1509 cm⁻¹, as the reference peak, the peak area ratios of A3415 to A1509 increased from 0.04 for SLS to 1.88 for LA. This was due to the contributions of the introduced amino groups in LA (see Figure 1).27 Moreover, the peak of aromatic C−H stretching vibrations, at ~817 cm⁻¹, for LA became much wider compared to that for SLS, indicating that the substitution reaction occurred on the benzene ring of lignin via the Mannich reaction.24 Table 1 shows the elemental compositions of SLS and LA. The nitrogen content increased from 0.07% for SLS to 6.49% for LA. Moreover, the amount of primary amine groups in LA was found to be 1.67 mmol/g. All of the results also indicate that amine groups were successfully introduced into the lignin structure.
Synthesis and Characterizations of Lignin Amine Hydrogel (LAH).

Scheme 2 illustrates the likely chemical reactions involved in the formation of a hydrogel network structure from LA and PEGDGE. It is known that the primary amino groups can easily open the epoxy ring through nucleophilic substitution. As the reaction proceeded, the
multifunctional LA and difunctional PEGDGE quickly formed an infinite polymer network. The amino groups introduced into lignin are believed to be much more reactive toward the epoxy groups of PEGDGE than the original hydroxyl groups in lignin.

**FTIR Spectra.** Figure 2 shows a comparison of the FTIR spectra of PEGDGE, LA, and LAH. There are some clear differences in the whole range of wavenumbers. The appearance of two new bands in LAH at 1114 and 951 cm\(^{-1}\), which were attributed to the C–O–C stretching vibration, clearly indicated the presence of PEGDGE segments in the hydrogel.\(^{27}\) The inclusion of the PEGDGE moiety in the hydrogel was also supported by increases in the absorbance of the bands between 2850 and 2910 cm\(^{-1}\), which originated from the C–H stretching of methylene in PEGDGE. Furthermore, new bands at 1353 and 848 cm\(^{-1}\), corresponding to the C–H bending vibration, and at 1252 cm\(^{-1}\), corresponding to the C–C stretching vibration, were also observed in the LAH hydrogel.

By comparing the spectra of LA and LAH, it is noted that the absorbance at \(\sim 3400\) cm\(^{-1}\), which was attributed to the stretching vibration of the hydroxyl groups and amino groups, showed little change. This is because the crosslinking reaction between the amino group of LA and epoxy group of PEGDGE also resulted in the formation of a new hydroxyl group; therefore, the intensity of the peak at 3400 cm\(^{-1}\) for LA and LAH did not change obviously.

**Solid-State \(^{13}\)C NMR.** Solid-state \(^{13}\)C NMR is widely used for investigating the composition of the hydrogel network. In this work, it was also used for analysis of the chemical structures of LA and LAH. In Figure 3, it can be seen that all characteristic peaks in the spectrum of LA were retained in the spectrum of the gel (LAH). For example, the signals between 146.8 and 163.2 ppm were attributed to the C3 and C4 of the guaiacyl units and C3 and C5 of the syringyl units in the lignin structure. Carbons at positions 1, 2, 4, 5, and 6 of the guaiacyl unit and other phenolic units (like 5-S, \(\beta\)-S, etc.) were noted in the peaks at 108.0–146.8 ppm. The peaks between 53.6 and 67.2 ppm were mainly attributed to the carbons of methoxy groups.\(^{28,29}\) However, a strong peak at 75.7 ppm is noted in the spectrum of LAH and is believed to be due to the presence of the PEGDGE moiety in the hydrogel structure. After PEGDGE was crosslinked with LA, the peak attributed to the methylene group (carbon c, Figure 3) in PEGDGE was shifted from 69.5 to 75.7 ppm. The broadening of this peak in the hydrogel resulted from the complex environment surrounding those newly formed bonds in the structure of the lignin hydrogel. This result indicates that the crosslinking reaction effectively took place between LA and PEGDGE.

**Hydrogel Composition.** Difunctional PEGDGE played the role of a crosslinker, whereas multifunctional LA served as both a building block and a branching unit in the formation of a hydrogel network structure. The number average molecular weight of PEGDGE is 500 g/mol, which corresponds to an equivalent epoxy weight of 4 mmol/g, whereas the primary amine content of LA is 1.67 mmol/g. When the crosslinking reaction proceeded by a stoichiometry of 1 M primary amine reacting with 1 M epoxy under the experiment conditions, the equivalent weight ratio of LA/PEGDGE was \(\sim 2.4/1\) (w/w). Consequently, the resulting hydrogel would assume a composition containing \(\sim 71\) wt % lignin. Figure 4 shows that the conversion of LA in the crosslinking reaction slowly decreased with an increase in the LA/PEGDGE weight ratio from 1.5/1 to 2.5/1, and there was a sharp drop on further
increasing the LA/PEGDGE ratio. On the other hand, the gel content remained almost unchanged with an increase in the LA/PEGDGE weight ratio to 2.5/1, which also similarly exhibited a rapid decrease with further increase in the LA/PEGDGE ratio.

When LA was in stoichiometric deficit (LA/PEGDGE = 1.5/1 to 2.5/1 w/w), it mostly reacted as indicated by the high LA conversion (Figure 4). Meanwhile, the resulting hydrogels exhibited a high level of gel content. In the case of LA in deficit, the higher than stoichiometric amounts (with respect to those of the primary amines) of the PEG moiety (Figure 5) in the resulting gels suggest that PEGDGE also reacted with other functional groups in addition to amino groups in LA. It is understood that both the primary amines and phenolic hydroxyl groups in LA can react with the epoxy groups of PEGDGE, but the primary amine groups have a higher reactivity.

When the LA/PEGDGE weight ratio was 2.5/1 (w/w), which was around the equivalent weight ratio (~2.4/1 w/w), besides showing a high conversion and gel content, the resulting gel exhibited a composition (69.6 wt % lignin) similar to that anticipated for the gel prepared by reaction of a primary amine and epoxy by stoichiometry (Figure 4). This result suggests that the reaction between the primary amines of LA and epoxy groups of PEGDGE proceeded to better completion. However, when LA in the reaction became increasingly excessive (LA/PEGDGE weight ratio >2.5/1), that is, the crosslinker was in greater deficit, the LA conversion and gel content of the resulting gels precipitated quickly (Figure 4). Nonetheless, in this case, the lignin contents in the resulting gels remained relatively unchanged (Figure 5). This evidence further supports the fact that the crosslinking reaction occurred mainly between the primary amines and epoxy groups.

In Figure 5, the LA content in the final product, LAH, increased from 63.2 to 69.6% with an increase in the LA/PEGDGE weight ratio from 1.5/1 to 2.5/1 in the crosslinking reaction; it then started leveling off at higher ratios. Again, this result suggests that beyond the stoichiometric amount excessive LA was largely not incorporated into the network structure. The highest LA content that could be achieved for the hydrogel in this study was around 71 wt %, which is almost identical to the composition of the hydrogel in which all primary amine groups were reacted with the epoxy group of PEGDGE in a 1:1 ratio.

Swelling and Interior Morphology of the Freeze-Dried Hydrogel. Figure 6 shows the swelling capacities of hydrogels with different LA contents. All hydrogels exhibited a significantly higher swelling capacity than that of similar SLS-derived hydrogels reported in the literature, suggesting that our preparation method of lignin-based hydrogels using LA could greatly improve the ability of water absorption. It is interesting to note that the swelling capacity of LAH increased continuously from 31 to 42 g/g with an increase in the LA content in the gel from ~63 to ~71 wt % (Figure 6) and then quickly leveled off with further increase in the LA content of the hydrogel. It is interesting to note that the gels containing higher PEG contents (or PEG-rich) in their structures exhibited lower swelling capacities. In contrast, gels with a composition similar to that anticipated by the stoichiometric reaction of primary amine/epoxy displayed the maximum swelling. This result suggests that for those PEG-rich gels some of the PEG chains were probably not effectively built into the network structure, that is, they were the dangling chains. The rheological properties shown below provided further support for this argument.

Figure 7 shows the interior morphological structures of freeze-dried LAHs with different LA contents. The honeycomb-like morphological structure of the freeze-dried hydrogel is a consequence of phase separation of water and the crosslinked polymer in the swollen hydrogel during drying, and the pore size is influenced by the chemical composition, crosslinking, and drying conditions. It was noted that the pore size of the xerogel increased with LA content in the hydrogel. The rigid aromatic LA building block might exhibit a higher tendency to aggregate with the evaporation of water during freeze-drying. Consequently, the swollen hydrogel with a higher LA content tended to phase-separate faster during drying, resulting in a coarse (large pore size) phase structure. Rheological Properties. The hydrogel specimens for rheological tests were prepared by transferring 1 mL of the reaction mixture into a disk-shaped mold and letting the gel form in the mold. The samples without extraction were used directly for rheological testing. The LAH gels exhibited typical
viscoelastic behavior, as both the storage modulus ($G'$; Figure 8a) and loss modulus ($G''$; Figure 8b) increased with oscillating frequency. $G'$ was larger than $G''$ over the whole range of frequencies, suggesting a general dominance of the elastic response of the gels to deformation over a broad time scale. It was noted that both $G'$ and $G''$ increased with an increase in the LA content of the LAH hydrogels, which was probably due to the improvement in the network structure of these samples and the more rigid molecular structure of the lignin moiety in the hydrogel network structure. Figure 8c shows the shear stress versus shear strain curves of LAHs with different LA contents. Whereas all hydrogel samples demonstrated similar strains at failure (~60%), they exhibited very different moduli and strengths, both of which increased rapidly with an increase in
the LA content of the gel. The inferior viscoelastic performance and shear mechanical properties for those PEG-rich hydrogels were likely due to the existence of network defects, like dangling PEG chains, as aforementioned. In addition, the rigid LA building block tended to render the hydrogel the superior mechanical performance.

EXPERIMENTAL SECTION

Materials and Methods. All chemical reagents were commercially available. SLS (M_w = 4000−100 000 g/mol, sulfonate salt content = 1.25−2.5 mequiv/g) was purchased from Borregaard Ligno Tech USA Inc. (Houston) and used as received. Sodium hydroxide (NaOH) was purchased from Macron Fine Chemicals, DETA (99.5% solution) from Acros Organics, formaldehyde (HCHO, 37% solution) from Fisher Scientific, hydrochloric acid (HCl, 36.8% solution) from EMD Millipore, and propanol and PEGDGE (M_n = 500 g/mol, density at 25 °C = 1.14 g/mL) from Sigma-Aldrich.

Preparation of LA. The preparation of LA followed a method reported in the literature.²² 10 g of SLS (OH value = 2.9 mmol/g) was first dissolved in 100 mL of distilled water in a three-necked flask equipped with a reflux condenser and a thermometer, and then, 15 g of DETA was added dropwise under stirring at room temperature. The pH of the solution mixture was adjusted to 10−10.5 using a 0.1 M NaOH solution and 0.1 M HCl solution. Next, 10 g of formaldehyde solution (37%) was added dropwise under stirring at room temperature. The temperature was raised to 50 °C and the reaction was continued for 4 h. Finally, the solution was poured into 500 mL of propanol to precipitate the LA. After the dark brown LA was collected by filtration and washed with propanol three times, the solid product was dried in a vacuum oven at 40 °C until a constant weight was reached. Primary, second, and tertiary amine groups are all likely present in the structure of the resulting LA. The primary amine is believed to be the most reactive form in the crosslinking reaction with the epoxy group of PEGDGE. The primary amine value of LA was determined according to the ASTM D 2074-92 and ASTM D 2074-92 methods, which are based on the formation of a Schiff base from the reaction of a primary amine and aldehyde. Salicylaldehyde was used the aldehyde reagent, and the primary amine content was determined by comparing the hydrochloride titration results before and after the reaction. The primary amine value was found to be 1.67 mmol/g.

Preparation of LAH. First, a predetermined amount of LA was dissolved in 10 mL of distilled water at 85 °C for 2 h under stirring. Next, to this LA solution was added PEGDGE (1 g) while stirring, and then the magnetic stirring was stopped. The hydrogel was formed in about 5 min. After the hydrogel was extracted thoroughly with warm and cold water until neither lignin nor PEGDGE was detected in the washing water by UV spectroscopy, the sample was freeze-dried.

Characterization and Tests. The content of LA in the hydrogels and its conversion efficiency were calculated using the following equations (eqs 1 and 2)

$$\text{LA}\% = \frac{(m_i - m_w)}{m_x} \times 100$$

$$\text{Y}\% = \frac{(m_i - m_w)}{m_i} \times 100$$

where LA% is the content of LA in the final hydrogel after the crosslinking reaction; Y% is the conversion efficiency of LA after the crosslinking reaction; m_i is the initial amount of LA added in the crosslinking reaction; m_w is the amount of LA in the washing water; and m_x is the weight of the xerogel after freeze-drying.

Figure 8. Storage modulus (G', 1% strain) (a), loss modulus (G'', 1% strain) (b), and stress−strain curves (1 Hz) (c) of LAHs with different LA contents. All of the gel test specimens contained 71.4% water.
concentration. A standard curve of the absorbance intensity at 280 nm versus SLS concentration was first established and then used for calculation of the mass of the residual SLS in the extraction water.\textsuperscript{23}

The gel content was calculated using eq 3

\[
X\% = \frac{m_s}{m_b} \times 100
\]  

(3)

where \(X\) is the gel content of LAH; \(m_s\) is the weight of the xerogel after washing; and \(m_b\) is the weight of the xerogel before washing.

**FTIR Spectroscopy and Elemental Analysis.** All samples were freeze-dried for 24 h prior to FTIR spectroscopy, solid-state \(^{13}\text{C}\) NMR spectroscopy, elemental analysis, and SEM measurements. FTIR spectra were obtained on a Nicolet Nexus 670 Fourier transform infrared spectrometer using the ATR mode of measurement. The samples were scanned 32 times in the range of 4000–650 cm\(^{-1}\). Element analysis was performed using a LECO CHN Analyzer according to the method of ASTM D5291.

**SEM.** After the hydrogel samples were swollen in distilled water at room temperature for 24 h, they were frozen in liquid nitrogen and then cut immediately into smaller samples with flat surfaces, followed by freeze-drying. Prior to the SEM experiment, the surface (cross-section) of the hydrogel was sputter-coated with gold. SEM examination was performed on an FEI Quanta 200F apparatus, with an accelerating voltage of 20 kV.

**\(^{13}\text{C}\) NMR.** Solid-state \(^{13}\text{C}\) NMR analysis for LA and LAH was performed on a Varian Inova 500 MHz NMR spectroscope equipped with a Nalorac H(CP)N Quad Resonance probe with XYZ-axis PFG. The \(^{13}\text{C}\) NMR spectrum of PEGDGE in D\(_2\)O was recorded using a Varian VNMRS 600 instrument.

**Swelling Capacity of Hydrogels.** A known weight of the xerogel placed in a tea bag was immersed in distilled water. After the sample was fully swollen without any stress at room temperature, the tea bag was removed from the water and the swollen hydrogel was filtered through a sintered-glass funnel to remove excess water. The swelling capacity of the hydrogel is calculated using eq 4

\[
\text{swelling capacity} = \frac{(W_s - W_d)}{W_d}
\]  

(4)

where \(W_s\) and \(W_d\) represent the weights of the swollen and dry hydrogel (xerogel), respectively.

**Rheological Measurement.** The rheological properties of the LAHs were measured using a Discovery HR-2 rheometer (TA instruments). A parallel-plate geometry with a diameter of 25 mm was used, and the testing gap was set at 2.0 mm. The angular frequency was scanned from 0.1 to 450 rad/s at 25 °C. The hydrogel test specimens were prepared by transferring aliquots of the reactant solution into a mold with disk-shaped cavities and letting the gel form in the mold at 85 °C. The disk-shaped cavities had the same diameter (25 mm) as that of the parallel plate and a thickness of 2 mm.

**CONCLUSIONS**

A new preparation method for lignin-based hydrogels was successfully introduced in this study. SLS was converted into an LA compound, which was then crosslinked using poly(ethylene) glycol diglycidyl ether to give hydrogels. Compared with the hydrogel counterparts prepared from unmodified lignosulfonate in the literature, the hydrogels in this study exhibited clearly higher conversions of lignin and gel contents. This was because the amine groups introduced, especially the primary amine groups, had a higher reactivity than the phenolic hydroxyl groups in the crosslinking reaction with the epoxy groups; consequently, the reaction efficiency for hydrogel preparation was greatly improved. Our LAHs also exhibited a higher swelling capacity than other similar lignin-based hydrogels in the literature. The lignin content in the resulting hydrogel increased with an increase in the LA/PEGDGE weight ratio in the reaction until it reached a maximum (~71 wt %); it then leveled off with further increase in the LA/PEGDGE ratio. It is noted that the maximum achievable lignin content in the hydrogel corresponded fairly well to the composition predicted by the stoichiometric reaction between the primary amines of LA and epoxy groups of PEGDGE in a 1:1 molar ratio. This result strongly suggests that formation of the hydrogel network structure was largely dictated by the reactions between the primary amines and epoxy groups. On the other hand, those gels with lignin contents lower than the maximum indicate that other functional groups in LA could also participate in the reaction process when primary amines are insufficient. However, the low swelling and rheological properties for those gels suggest the existence of network defects, probably some dangling PEG chains. Nonetheless, all gels with a similar lignin content as that predicted by the stoichiometric reaction between primary amines and epoxy groups exhibited superior swelling capacity, viscoelasticity, and shear properties, suggesting improvement of the network structures in these gels. The results from this study suggest that converting lignosulfonate to the more reactive LA and subsequently crosslinking it with a diglycidyl ether compound is a good method for the preparation of lignin-based hydrogels with an improved performance.

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**Notes**
The authors declare no competing financial interest.

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