Preparation and Properties of Kraft Lignin-N-Isopropyl Acrylamide Hydrogel

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Kraft lignin was used to prepare kraft lignin-N-isopropyl acrylamide hydrogel (KNIAH). The results indicated that using a 1:2 mass ratio of KL-to-N-isopropyl acrylamide (NIPAM), 48 h reaction time, and 1.5 mL of crosslinking agent yielded KNIAH with the maximum swelling degree (209.3%). The crosslinking reaction was verified by C-N shifting at 1272 cm\(^{-1}\) and increased C=O bonding at 1720 cm\(^{-1}\). KNIAH with a smooth and uniform surface was created. DSC demonstrated that free water combined with KNIAH at 200 °C, after which KNIAH began exothermic decomposition. TGA shows that KNIAH with good performance of heat resistance and degradation. Absorption was maximized at 20 °C; low temperature and neutral solution was conducive to water absorption. Decolorization increased with decreasing concentration and pH value.

Keywords: Gels; Grafting; Copolymers; Crosslinking

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INTRODUCTION

Lignin is the primary by-product from the preparation of pulp for papermaking, and it is found in the black liquor from the pulping process. It has excellent performance, high reactivity, good biocompatibility, and degrades easily to displace other phenolic compounds in formaldehyde-based adhesives (Gao et al. 2013). Kraft lignin extract from kraft straw black liquor collected using acid precipitation is typically negatively charged when in solution, and thus has the characteristics of an anionic surfactant (van Vlierbergh et al. 2011). Lignin is an attractive candidate in hydrogels because of its advantages due to their inherent properties such as biocompatibility, biodegradability, low toxicity, and eco-friendliness (Vijay et al. 2013, 2015). Feng et al. (2012) and El-Zawawy (2005) discovered that lignin introduced into resorcinol or polyvinyl alcohol creates a hydrogel, enhancing the hydrogel’s performance stability and biocompatibility compared with that without lignin. Kraft lignin can be made into a hydrogel in the form of an interpenetrating or semi-interpenetrating polymer network (IPN) to improve the hydrogel swelling degree and performance reliability (Li et al. 2010).

Hydrogels typically exhibit three-dimensional networks that affect absorption (Wang et al. 2010). N-isopropyl acrylamide (NIPAM) is widely utilized in studies as an environmentally-sensitive hydrogel because it is easily prepared and useful for such applications (Wang et al. 2005; Liu et al. 2013). Uraki et al. (2006) and Nishida et al. (2003) previously utilized NIPAM as a raw material to prepare hydrogels with good sensitivity to temperature. However, the swelling degrees of their hydrogels were low and they exhibited poor stability.
To improve the performance stability of hydrogels, the present work adopted NIPAM and KL as raw materials. Ammonium persulfate was used to initiate this double bond in the molecular structure of NIPAM grafted with the phenolic –OH group of lignin to prepare the copolymer (KNIAC) by graft copolymerization and to form a kraft lignin-N-isopropyl acrylamide hydrogel (KNIAH) after cross-linking using glutaraldehyde. FTIR, Kjeldahl, SEM, and DSC were used to characterize KNIAH, detect the environmental sensitive properties, and evaluate its capacity to adsorb methylene blue.

**EXPERIMENTAL**

**Materials**

The materials utilized in this work include kraft lignin (KL), a brown powdery substance with a distinct odiferous nature, a by-product of the papermaking industry, as well as various reagents including ammonium persulfate, sodium hydroxide, acetone, 50% glutaraldehyde, N-isopropyl acrylamide (NIPAM), and methylene blue. The instruments used in this work include an FT-IR-650 Fourier transform infrared spectrometer and a DF-4 tablet machine produced by Tianjin Port East Technology Development, Ltd., and by Share Ltd., China, respectively. A KDY-9810 Kjeldahl apparatus, produced by Beijing Think Better Electromechanical Technology Research Institute, China, was used. A TU-1901 double-beam UV spectrophotometer, produced by Beijing Purkinje General Instrument Co., Ltd., China, was also used.

**Methods**

**Preparation of KNIAH**

KL was dissolved in NaOH solution with pH at 10. Ammonium persulfate was added with NIPAM and the mixture was stirred for 2 h under the reaction temperature at 70 °C. The reaction solution was concentrated via acetone sedimentation and repeated extraction and vacuum-dried for 24 h at 40 °C to obtain the monomer (Zhang et al. 2009), KNIAC. The KNIAC was dissolved in distilled water at 1.0% mass concentration. 10 mL of the solution was removed from the container and a cross-linking agent, glutaraldehyde, was added at room temperature (25 °C) to form KNIAH (Singh et al. 2006).

**Measurement of IR spectrum**

The hydrogel was dried to constant weight and mixed with a sample of KBr at a 1:200 ratio. Next, it was tabletted by a DF-4 tablet machine and kraft lignin-N-isopropyl acrylamide hydrogel was tested with the FTIR-650 apparatus.

**Determination of nitrogen content**

The nitrogen content of the hydrogel was evaluated according to Chinese National Standard GB/T5009.5-2003 (2003). After being dried to constant weight, the hydrogel nitrogen content was determined using the KDY-9810 Kjeldahl apparatus.

**Scanning electron microscopy (SEM) examination**

The surface morphology of KNIAH was examined using a Quanta200 Electron Microscope after it was dried to constant weight. KNIAH was gold-coated prior to microscope observation.
**Differential scanning calorimetry (DSC)**

KNIAH was dried to constant weight and a DSC was performed using a NETZSCH DSC204 apparatus under a nitrogen atmosphere at a flow rate of 15 mL/min. The heating rate was 10 °C/min though the temperature ranges of 25 to 300 °C.

**Thermogravimetric analysis (TGA)**

The thermal properties of kraft lignin, KNIAC, and KNIAH were measured using thermogravimetric analysis (TGA). In preparation of samples for TGA, the hydrogels were ground to powder form. Decomposition profiles of TGA were recorded at a heating rate of 10.0 °C/min between room temperature and 600.0 °C in nitrogen.

**Swelling capacity**

The swelling ratios of KNIAH were measured according to the methods of Chang and Lin (2000): A dried piece of KNIAH was placed in water at room temperature for 24 h, the KNIAH swelled and reached equilibrium, the KNIAH was removed and surface water was removed with filter paper, and finally, the weight of the wet KNIAH was calculated using the following equation,

\[
S = \frac{(W_s - W_d)}{W_d}
\]

where \(W_s\) is the wet KNIAH weight and \(W_d\) is dry KNIAH weight.

**Adsorption properties on methylene blue**

The adsorption properties of kraft lignin-N-isopropyl acrylamide hydrogel (KNIAH) on methylene blue were measured according to methods described by Uraki et al. (2006): KNIAH (0.1 g) was added to a concentrated methylene blue solution (0.02 L) and the pH was adjusted. The mixture was stirred for 2 h until adsorption equilibrium was achieved, at which point the supernatant was tested. The adsorption amount was calculated as follows,

\[
Q = (c_0 - c_1) \times 0.02/m
\]

where \(c_0\) is the KNIAH concentration before adsorption, \(c_1\) is the KNIAH concentration after adsorption, and \(m\) is the weight of KNIAH.

**RESULTS AND DISCUSSION**

**The Main Functional Group Content of KL**

According to the determinate method of the literature (Ren et al. 2008), the results are as follows: The experiment measured the acid-soluble kraft lignin content as 1.2% (mass percentage), the ash content as 14.27%, and the Klason lignin content as 64.55%. Table 1 presents the main functional group contents of KL.

<table>
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<th>Table 1. Characteristics of the KL Studied</th>
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<td><strong>Content</strong> (mass, %)</td>
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Preparation of KNIAH

In the presence of the ammonium persulfate initiator, the double bond in the molecule NIPAM initiates polymerization, and graft polymers are formed via H atom substitutions for hydroxyl groups on the lignin molecular chain and the more-reactive amino group (Feng et al. 2011). Glutaraldehyde is highly active, fast-responding, and has high binding capacity and product stability. As the cross-linking agent, glutaraldehyde can act as a bridge for cross-linked polymer materials, forming a polymer compound with a well-developed pore structure (Parajuli et al. 2005). The aldehyde can cross-link with the amino copolymer to generate N⁺, preparing the KNIAH. The reaction mechanism describing the preparation of the hydrogel is presented in Fig. 1.

\[
\text{Fig. 1. The synthesis mechanism of KNIAH}
\]

**Mass ratio of Kraft lignin-to-N-isopropyl acrylamide**

Figure 2 shows the effects of Kraft lignin-to-N-isopropyl acrylamide mass ratio on the swelling degree of KNIAH prepared with 48 h reaction time, 1.5 mL of glutaraldehyde, at 25 °C. Under alkaline conditions, the ortho α-H groups of KL exhibit high reaction activity with the same NIPAM reaction mechanism. KL is a high-molecular weight polymeric material with high relative content and steric hindrance which did not facilitate the reaction.

\[
\text{Fig. 2. Effect of Kraft lignin and N-isopropyl acrylamide mass ratio on swelling capacity of KNIAH}
\]
Increasing the NIPAM content can enhance the binding ability of the raw material, the graft point and grafting efficiency, and then increase the reaction volume and the swelling degree. When the NIPAM was too high, the graft point tended towards saturation and NIPAM homopolymerization occurred, surrounding the partial monomer. This in turn decreased the amount of hydrogels macromolecular chain that were produced under the action of the crosslinking agent, and the swelling degree sharply declined. The most effective mass ratio of kraft lignin and NIPAM was 1:2.

**Reaction time**

At a constant glutaraldehyde volume (1.5 mL), temperature (25 °C), and mass ratio of kraft lignin-to-N-isopropyl acrylamide (1:2), the swelling capacity as a function of cross-linking time is shown in Fig. 3. With the extension of reaction time, the swelling degree of the hydrogel rose slightly. The hydrogel has smaller steric hindrance in the preliminary stage and cannot form a half-interpenetrating network structure that is propitious to the crosslinking reaction. As the reaction continued, the molecular polymer participating in the reaction increased. A network structure was generated, increasing swelling degree. When the crosslinking time exceeded 48 h, steric hindrance became aggrandized, the cross-linking degree reached saturation, and water molecule penetration was abated. Further extending the cross-linking time had little effect on the KNIAH swelling degree. The cross-linking time of 48 h was selected to maximize production efficiency and minimize production costs.

![Swelling capacity vs crosslinking time](image)

**Fig. 3.** Effect of reaction time on swelling capacity of KNIAH

**Glutaraldehyde content**

Under constant reaction time (48 h), temperature (25 °C), and kraft lignin-to-N-isopropyl acrylamide mass ratio (1:2), the swelling degree as a function of glutaraldehyde usage is shown in Fig. 4. Using glutaraldehyde to prepare the hydrogel destroyed intermolecular hydrogen bonding and the intermolecular copolymer, which normally combine to form the semi-interpenetrating amino copolymer. Thus, the hydrogel was prepared with semi-IPN. By decreasing the glutaraldehyde usage, KNIAH was created with low cross-linking degree but high steric hindrance, so forming a network structure was difficult and did not favor the reaction. By increasing the amount of glutaraldehyde,
a network structure was formed and the molecular chain structure of hydrogel was destroyed, so the hydrogel’s swelling degree increased. As cross-linking reached a maximum, the cross-link density grew and the molecular distance between network points was lower. As the network structure was filled, the swelling ratio decreased. The experimental results are consistent with those of Zhao et al. (2008).

Fig. 4. Effect of glutaraldehyde content on swelling capacity of KNIAH

FT-IR Spectra

FTIR spectra for KNIAH are presented in Fig. 5. The peak at 1720 cm\(^{-1}\) is the C=O stretching absorption peak, the absorption peak of C-N stretching vibration is at 1272 cm\(^{-1}\), and the C-N stretching vibration peak is at 1265 cm\(^{-1}\) (Chauhan et al. 2004). The unreacted NIPAM and KL were removed by repeated washing. The C-N stretching vibration absorption peak at 1265 cm\(^{-1}\) was observed, indicating that KL and NIPAM were well cross-linked. The C=O stretching absorption peaks at 1720 cm\(^{-1}\) increased in intensity significantly, as indicated by the reaction mechanism as C=O bonds were introduced. While the C-N stretching vibration absorption peak at 1272 cm\(^{-1}\) offset may be observed, copolymers were cross-linked with glutaraldehyde and KNIAH.

Fig. 5. FT-IR spectra of KNIAH
Nitrogen Content

Analysis with the Kjeldahl nitrogen instrument, via digestion-distillation-titration, measured the nitrogen content of KL as 0.85% and that of KNIAH as 4.06%, which is smaller deviations compared with theoretical prediction (4.26%). NIPAM not involved in the reaction was removed by washing.

SEM Analysis

SEM images of KNIAH are presented in Fig. 6. Based on a comparison of images (a) and (c), the KNIAC section had a more uniform pore structure and higher porosity, whereas the KNIAH section exhibited a relatively smooth and well-proportioned network structure with dense architecture and without any apparent microscopic phase separation. Images (b) and (d) reflected the surface morphology of the two substances. KNIAC had a non-continuous, closed-mesh structure and an uneven surface with significant concavity. The irregular pore structure of KNIAH provided channels for molecular flow and exhibited a smooth surface, reflecting the molecular glutaraldehyde hydrogel after absorbing water.

![Fig. 6. SEM images of KNIAC and KNIAH under different magnification: (a) section of KNIAC; (b) surface of KNIAC; (c) section of KNIAH; and (d) surface of KNIAH](image-url)

DSC Analysis

Figure 7 shows DSC curve of KNIAH. KNIAC and KNIAH both exhibited one endothermic peak and one exothermic peak. The endothermic peak of KNIAH grew
larger due to the water in the intramolecular structure. Moisture evaporation absorbed heat within the temperature range of 50 to 100 °C, decreasing the exothermic peak at 180 °C. The temperature corresponding to the maximum rate was relatively low. The endothermic peak appeared in two sharp copolymer peaks, with three types of water existing in the copolymers: free water, intermediate water, and non-freezable water (Baba et al. 2004). The temperature of the endothermic phase transition was high because KNIAH retained existing free water and middle water, which contributed to its structural stability. As the phase transition occurred at 270 to 320 °C, heat release increased and molecular structure damage occurred. KNIAH stability was reduced by exothermic decomposition when the temperature exceeded 320 °C.

**Fig. 7.** DSC curves of KNIAC and KNIAH

**TGA Analysis**

The thermal degradation behavior of the hydrogels was studied in the range 25 to 600 °C under a nitrogen atmosphere. The thermogravimetry curves obtained with kraft lignin, KNIAC, and KNIAH are presented in Fig. 8. The first phase of the weight loss (25 to 150 °C) indicates evaporation of smaller molecules and shows that heat-resistant properties of KNIAH were improved.

**Fig. 8.** TGA curves of KNIAC and KNIAH
For kraft lignin, the vast majority of the weight loss occurred at higher than 200 °C, with the maximum decomposition rate at 320 °C. For KNIAC, there are two decomposition phases, with maximum decomposition rate at 360 °C. The maximum decomposition rate of KNIAH occurred at 245 °C. The residual rate of KNIAH was much lower than that of kraft lignin and KNIAC, which indicates that the KNIAH with thermal degradation.

Response of Hydrogel to Environment

Hydroxyl radicals, as a hydrophilic functional group, generally have excellent water absorbing character. The O-H vibration peaks clearly indicated that KNIAH had excellent water adsorption performance (Cha et al. 2012). The response of hydrogels in water is demonstrated in Fig. 9. Figure 9A shows the effect of concentration on the adsorption capacity of KNIAH, while Fig. 9B shows the influence of pH. The temperature sensitivity was attributable to the branches of N-isopropyl molecules; repeated swelling and contracting did not occur as the temperature changed (Kim and Kadla 2010). At low temperatures, water activity was inhibited and swelling was poor. When swelling reached a maximum and temperature rose further, the sensitivity did not markedly change.

The hydrogel network shrinks in acidic solution, inhibiting water molecules from entering the gel and then reduces the swelling degree. By increasing the pH, ionic strength is increased, decreasing shrinkage of the hydrogel network structure and increasing the internal molecular osmotic pressure from the C═O and N—H in the molecules. This creates a more conducive environment for water adsorption into the molecules. When the pH exceeded 7, ionic strength gradually decreased and the molecular osmotic pressure was reduced. Water absorption and swelling were highest at relatively neutral pH.

![Fig. 9. Response of hydrogel to the environment: (A) effect of concentration; (B) effect of pH value](image)

Adsorption Properties on Methylene Blue in Different Temperature and pH

KNIAH adsorption of methylene blue dye is demonstrated in Fig. 10. Figure 10A shows the effect of concentration on the adsorption capacity of KNIAH and Fig. 10B shows the influence of pH. From the IR spectra, it is known that KNIAH contains a large number of N atoms which hydrogen-bond and facilitate adsorption of the dye. Hydrogels can produce electrical attraction to the dye, further facilitating dye adsorption.
(Vijayaraghavan et al. 2008; Liu et al. 2011). Hydrogels have a three-dimensional network structure which favors adsorbed molecules. When the dye concentration was low, the dye molecules made contact with the nitrogen atoms of the hydrogel, producing the hydrogen bond that triggers the adsorption effect. When the dye concentration increased, methylene blue molecules in the hydrogel adsorbed to nitrogen atoms in the molecules. Higher dye concentration allows for greater contact and higher adsorption capacity. When the dye concentration reached a certain value, adsorption onto the hydrogel reached saturation and the dyes were densely distributed. The intermolecular electrical attraction was reduced as absorption of external methylene blue with the gel molecular. The carboxyl groups in molecular hydrogel can electrostatically attract cationic methylene blue. When the pH was low, H⁺ accumulated on adsorption sites with methylene blue and led to weak adsorption ability. The adsorption capacity decreased as the pH increased. The amount of H⁺ adsorption increased the competition between the hydronium ion and the dye ionic species for the adsorption sites. When the pH was neutral, competition decreased and hydrogel ionization yielded negative charges. Hydrogel adsorption electrostatic interaction thus promoted methylene blue adsorption.

![Graph A](image1.png)  ![Graph B](image2.png)

**Fig. 10.** KNIAH-methylene blue adsorption capacity: (A) effect of concentration; (B) effect of pH

**CONCLUSIONS**

1. The optimum kraft lignin-to-N-isopropyl acrylamide mass ratio, relative to the preparation of a high-swelling hydrogel, was 1:2. The cross-linking time was 48 h, and the usage of crosslinking agent was 1.5 mL. The maximum KNIAH swelling degree achieved 209.3%.

2. Occurrence of the graft reaction due to the C-N key and the cross-linked C-N bond shift increased, illustrating that KNIAH obtained through the cross-linking reaction.

3. The nitrogen content in the polymer was 4.06%, close to the theoretical value of 4.26%.

4. SEM revealed a crystalline KNIAH structure with a smooth, three-dimensional pore structure.

5. As shown by DSC, the hydrogel contained free water molecules, which exhibited an exothermic peak when the temperature exceeded 200 °C. TGA shows that KNIAH with good performance of heat resistance and degradation.
6. The performance of KNIAH was tested. Repeated swelling and contraction with temperature demonstrated no change. Water absorption was most efficiently at 20 °C, and elevated temperature hindered water absorption.

7. Neutral pH solutions were conducive to water absorption.

8. Methylene blue adsorption by KNIAH increased with methylene blue concentration and higher solution pH made the polymer more conducive to adsorption, until the pH became neutral and adsorption leveled off.

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