Synthesis and Characterization of Alkali Lignin-based Hydrogels from Ionic Liquids

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Hydrogels from alkali lignin were prepared and shown to display unique swelling. Variable lignin contents (6.25%, 10.00%, 12.50%, and 14.29%) were successfully grafted with both N,N'-methylenebisacrylamide (MBA) and acrylamide (AM). Ionic liquids such as 1-ethyl-3-methylimidazolium acetate ([Emim]Ac) were used to avoid harsh, unfriendly solvents. All materials were characterized using X-ray diffraction (XRD) FT-IR spectroscopy, scanning electron microscope (SEM), thermogravimetric analysis (TGA), and swellability. The swelling behaviors of the hydrogels were noticeably influenced by their lignin content. The degree of equilibrium swelling (the maximum swelling degree) decreased with increasing content of lignin. The highest swelling degree (1,650%) was obtained at 6.25 wt% lignin. Kinetics revealed that the swelling behaviors of hydrogels were well-fitted by the Schott model.

Keywords: Ionic liquids; Lignin; Hydrogel; Swellability

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INTRODUCTION

There is increased interest in natural polysaccharide-based hydrogels because of their biodegradable, renewable, and low-cost characteristics. They also have potential applications in wastewater treatment (Paulino *et al.* 2011), food (Chang and Zhang 2011), wound dressing (Liebner *et al.* 2007), drug delivery (Matricardi *et al.* 2013), and coatings (Hoepfner *et al.* 2008). Several other natural materials for the synthesis of hydrogels include chitosan (Berger *et al.* 2004), chitin (Hu *et al.* 2011), alginate (Augst *et al.* 2006), hyaluronic acid (Burdick and Prestwich 2011), and cellulose (Wang *et al.* 2012). Lignin, the second or third most abundant terrestrial polymer after cellulose, accounts for up to 30 wt% of wood (Singh *et al.* 2014). Worldwide production of approximately 26 million tons/year of lignin occurs primarily through chemical pulping (Kadla *et al.* 2002). Almost all of this lignin is burned to generate energy as a low-value heating fuel. To maximize its full value, lignin should be converted to high-value products (Matsushita and Yasuda 2005). In the past few decades, hydrogels from lignin have been intensively studied and applied in drug delivery (Lee and Yeh 2005), adsorbing metal ions (Parajuli *et al.* 2005), and temperature and pH-sensitive materials (Yang *et al.* 2011).

Lignin is a three-dimensional stereoscopic amalgamation of amorphous polyphenol monomers that cannot dissolve in common solvents (Lu and Ralph 2003; Jia *et al.* 2010; Yokoyama and Matsumoto 2010). Dissolution of lignin without any pretreatment and/or derivatization is critical for its valorization. Many technologies currently used to process lignin into a hydrogel employ harsh alkaline or acidic conditions (Yamamoto *et al.* 1999; Nishida *et al.* 2003) and/or organic solvents (Wu and Argyropoulos 2003; Uraki *et al.* 2004) that are generally less than ideal and lack environmental compatibility (Wu and Argyropoulos 2003; Zhao *et al.* 2009).

Ionic liquids (ILs) are liquids at or below 100 °C comprised entirely of cations and anions and have been touted as green solvents over the last few decades because they are reusable, non-corrosive, non-combustible, and operate under mild conditions (Zhu *et al.* 2006; Fort *et al.* 2007; Pu *et al.* 2007). Recently, ILs have been used as solvents for natural polymers including cellulose and starch (Li *et al*. 2008; Sun *et al.* 2014). The anions have a sufficiently strong coordinative ability to break the three-dimensional network structures of lignin (Luo *et al.* 2008).

In the present study, 1-ethyl-3-methylimidazolium acetate ([Emim]Ac) was used to dissolve lignin, after which the chemical properties and swelling behavior of the resultant hydrogel were evaluated.

EXPERIMENTAL

Materials

Eucalyptus chips from a paper mill in Shandong Province, China, were pulped. Lignin was obtained from the resultant kraft pulp following literature methods and placed in a vacuum oven (50 °C, 0.1 MPa) for 24 h (Wang and Chen 2013).

[Emim]Ac, with a purity of *ca*. 99.0%, was purchased from Shanghai Chengjie Chemical Co., China and was used as received without further purification. Acrylamide (AM) and N,N'-methylenebisacrylamide (MBA) were purchased from Aladdin Industrial Corporation (China). Other reagents were of analytical grade and used without further purification.

Methods

Preparation of lignin hydrogels

A specific amount of lignin and 10 mL of [Emim]Ac were added to a 50-mL glass flask. The system was stirred at the specified temperature under nitrogen until it became a stable suspension. Lignin-containing hydrogels (LCHs) were prepared by simple mixture and solution polymerization using initial solutions of monomers (lignin and AM), cross linkers (MBA), and initiators (H_2O_2-$CaCl_2$). Formulae for the syntheses of the LCH are listed in Table 1.

LCH_1, with 6.25% lignin, was prepared as follows: 0.10 g of lignin and 0.10 g of $CaCl_2$ were dispersed in 5.0 mL of [Emim]Ac in a 50-mL glass flask at 75 °C for 15 min. Subsequently, 1.5 g of AM, 0.10 g of MBA, and 70 μL of 30% H_2O_2 were added. The system was stirred at 75 °C until it became a solution. When the color of the solution turns brown, lignin is completely dissolved (Ji *et al.* 2012). The solutions were transferred into a glass tube for hydrogel formation under a blanket of nitrogen at 75 °C for 1.5 h without stirring. After hydrogel formation, the composite hydrogels, in their cylindrical form, were taken out and placed into deionized water to remove homopolymers, unreacted monomers, and [Emim]Ac. The ionic liquid was recovered through reduced pressure distillation. The lignin content was calculated as follows,

$$lignin\ (wt\%) = (m_0)/(m_0+m_1+m_2) \quad (1)$$

in which m_0, m_1, and m_2 represent the weight of the lignin, AM, and MBA, respectively.

Table 1. Formulae for the Synthesis of Lignin-Containing Hydrogels

Samples ID	LCH_1	LCH_2	LCH_3	LCH_4
Lignin (wt%)	6.25	10.00	12.50	14.29
AM (g)	1.5	1.5	1.5	1.5
MBA (g)	0.10	0.10	0.10	0.10

Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a VERTEX 70 (Bruker, Germany) in the range 500 to 4000 cm^{-1} at resolution of 0.5 cm^{-1}.

Scanning electron microscope (SEM)

The morphology of the surfaces of lignin was observed by SEM (Bruker, Germany) at 10 kV. The samples were prepared in the following manner: a freeze-dried sample was spread on a circular base with double-sided tape having high conductivity and covered with a thin layer of sputtered gold by magnetron sputtering equipment (approximately 2 nm) to promote conductivity before SEM observation.

X-ray diffraction (XRD)

XRD was conducted using a D8 ADVANCE X-ray diffractometer (Bruker, Germany) under the following conditions: tube current and voltage were 20 mA and 30 kV, respectively, Cu target, and data were collected over 2θ Bragg angles from 5 to 90 degrees at a scanning speed of $0.02^o\ s^{-1}$.

TGA analysis

The thermal stability of the samples was evaluated using thermogravimetric analysis (TGA) (TGA Q500, TA, USA). Samples of approximately 12 mg were heated in an aluminum crucible to 700 °C at a heating rate of 20 °C min^{-1} while the apparatus was continually flushed with a nitrogen flow of 25 mL min^{-1}.

Swelling property of LCH

The "weight method" was adopted to measure the swelling of hydrogel as follows: the dried hydrogels were immersed in distilled water for different times at 25 °C, after which they were removed from the water and their surfaces were blotted with filter paper before being weighed. The swelling ratio was calculated as follows,

$$SR = (M_t-M_0)/M_0 \quad (2)$$

in which SR, M_t, and M_0 represent the swelling ratio, the weight of the dried hydrogel, and the initial weight of the hydrogel, respectively.

RESULTS AND DISCUSSION

FT-IR and XRD Analysis

FT-IR spectra were used to identify changes in the functional groups (Fig. 1a). The characteristic FT-IR peaks at 1507 and 1595 cm^{-1} are attributed to benzene skeletal vibrations and C=O stretching vibration, respectively. The peaks at 1375 and 1275 cm^{-1} are attributed to lignin containing syringyl and guaiacyl units (Tejado *et al.* 2007; Laskar *et al.* 2013). In contrast to the original lignin, a new peak at 3200 cm^{-1} appeared in the FT-IR spectrum of the four hydrogels, which was attributed to the stretching band of the N-H bonds, confirming successful functionalization of lignin chains onto AM. The 1660 cm^{-1} band was due to the C=O stretching mode (Mai *et al.* 2000). These results support the contention that AM was copolymerized with lignin (Fig. 2).

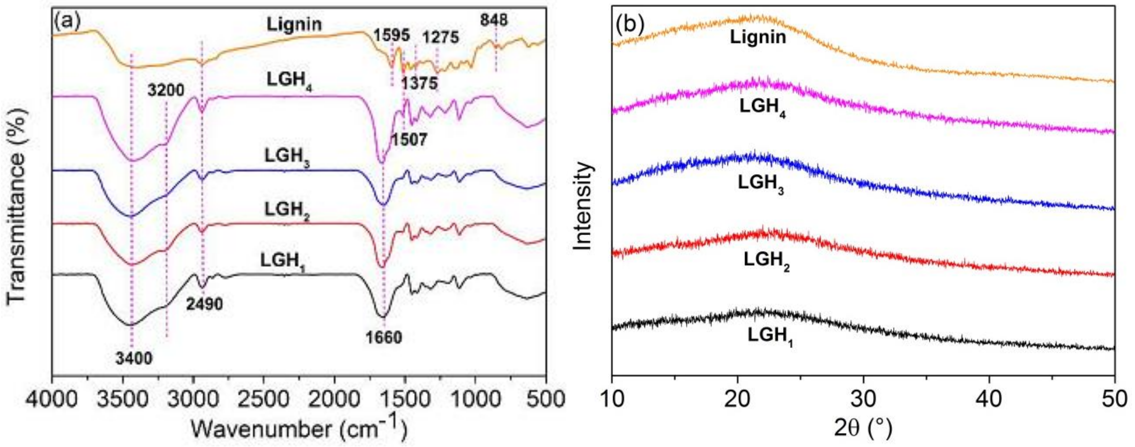

Fig. 1. FT-IR (a) and XRD (b) spectra of lignin and LCH_{1-4}

Fig. 2. Schematic diagram of the green synthesis of LCH

The aim of this work was to obtain a simple and green method to prepare lignin-containing hydrogels, thus to maximize full value of lignin. Therefor this research mainly studied the properties of LGHs, and all of the prepared hydrogel samples contained lignin. To better understand the crystalline nature of the hydrogels, XRD patterns of freeze-dried

LCH with varying lignin amounts were acquired (Fig. 1b). The hydrogels had a broad diffraction pattern with a peak value at approximately 2θ = 22°, which indicates the presence of a significant amount of amorphous substances, likely lignin.

Thermogravimetric Analysis

Because of the importance of thermal stability in many applications of composite materials, the thermal decomposition of the freeze-dried hydrogels was examined by thermogravimetric analysis (TGA) under nitrogen. The TGA and DTG curves of LCH$_{1-4}$ are shown in Fig. 3. The thermal properties of hydrogels with various amounts of lignin indicated that the lignin-containing hydrogels had the same degradation pattern. The hydrogels with different amounts of lignin had different onset temperatures (Table 2). A slight difference in degradation onset temperature of LCHs could be observed from the Table 2. The lowest onset temperature was observed for LCH$_1$ (~228 °C) and the highest onset was observed for LCH$_4$ (~245 °C). The incorporation of lignin into the hydrogels slightly improved the thermal stability, as evaluated from the thermal degradation temperatures at 50% weight loss ($T_{50\%}$) and the maximum decomposition temperature (T_{max}) (Table 2). The thermo-oxidative degradation value at 50% for LCH$_1$ was 368.76 °C, whereas the $T_{50\%}$ for LCH$_3$ was 383.01 °C, slightly higher than the value for LCH$_1$. The T_{max} for LCH$_1$ was 366.76 °C, while the T_{max} values for LCH with 10.00, 12.50, and 14.29 wt% lignin were 378.50, 378.67, and 374.04 °C, respectively. Therefore, the addition of lignin was beneficial to the thermal stability of LCH.

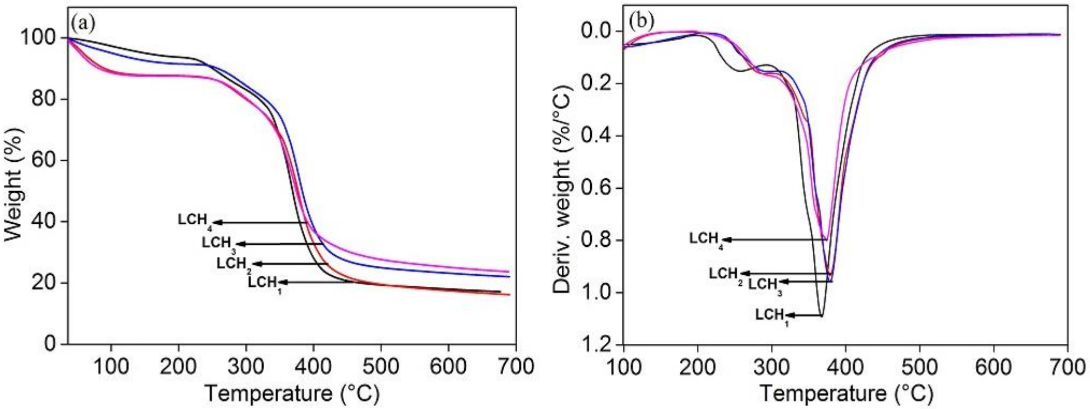

Fig. 3. (a) TGA and (b) DTG curves of LCH$_{1-4}$

Table 2. Thermogravimetric analysis of LCHs

Samples ID	Onset temperature (°C)	Temperature at maximum rate of wt. loss (°C)	Decomposition temperature (°C)
			50%
LCH$_1$	~228	366.76	368.76
LCH$_2$	~243	378.50	376.84
LCH$_3$	~240	378.67	383.01
LCH$_4$	~245	374.04	374.37

SEM Analysis

The hydrogel surface was observed by SEM after it was freeze-dried for 24 h. Figure 4 provides the SEM micrographs of LCHs with various contents of lignin. The surface of the hydrogel has many irregular pores with sizes of several micrometers to tens of micrometers. The hydrogels with different amounts of lignin were similar in structure. Overall, the average pore size of the LCHs decreased with increasing lignin content. One possible reason is that an increase in the number of hydrogen bonds between the OH groups of the lignin and AM units changed the continuous network. Besides, the decrease of the pore size may be related to the lower degree of swelling of the hydrogels with higher lignin content.

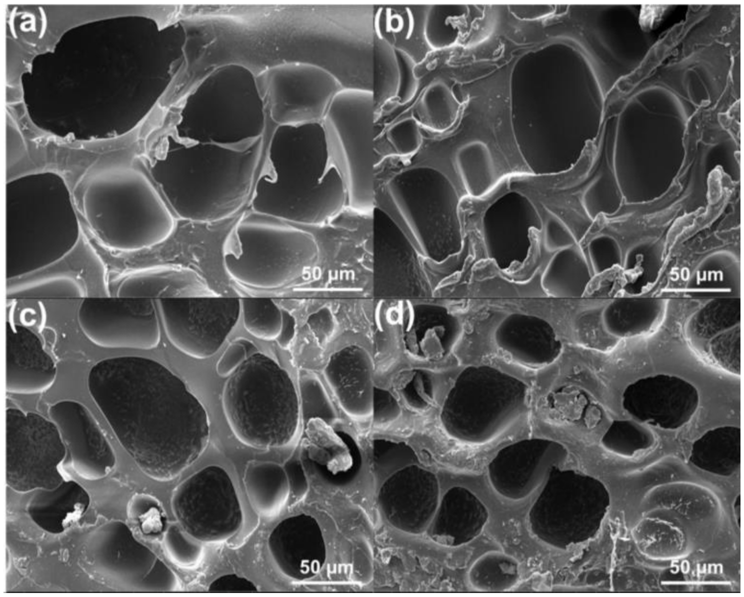

Fig. 4. SEM images of LCH samples: (a) LCH_1; (b) LCH_2; (c) LCH_3; (d) LCH_4

Swelling Behaviors of the Hydrogels

The swelling behavior was systematically investigated to provide new light on the structural features of the composite hydrogels. It is well-known that the swelling behaviors of hydrogels depend heavily on the cross-linked density of the gel network (Huang *et al.* 2012; Shen *et al.* 2012). In Fig. 5a, it can be seen that the swelling ratio of hydrogels first sharply increased and then remained constant with time. At 60 min, swelling equilibrium was achieved. Meanwhile, the swelling ratio of the LCHs decreased with increasing lignin content (Fig. 6). Possible reasons are as follows: (1) because lignin is hydrophobic, it can repel water; consequently, when the content increased, the hydrophobicities of the hydrogels increased; (2) as shown in the SEM images of LCH samples, an increase in lignin content can decrease the average pore diameter, thus decreasing the swelling ratio of the hydrogels.

Water diffusion of hydrogels and the rate of water diffusion are influenced by many factors, such as stress relaxation (Franson and Peppas 1983), cross-link concentration (Robert *et al.* 1985), and ionic groups (Suarez *et al.* 2009). To investigate the diffusion of the hydrogels, the initial swelling data were fitted by an exponential heuristic equation for $W/W_e \leq 0.5$ (Zhang *et al.* 2014),

$$W/W_e = Kt^n \tag{3}$$

which may be reorganized to obtain a linear form:

$$\lg(W/W_e) = n\lg t + \lg K \tag{4}$$

In Eqs. 3 and 4, W/W_e is the fractional water uptake by the hydrogel, t is the diffusion time, k is a constant characteristic of the system, and n is an exponent characteristic of the mode of transport of the penetrant.

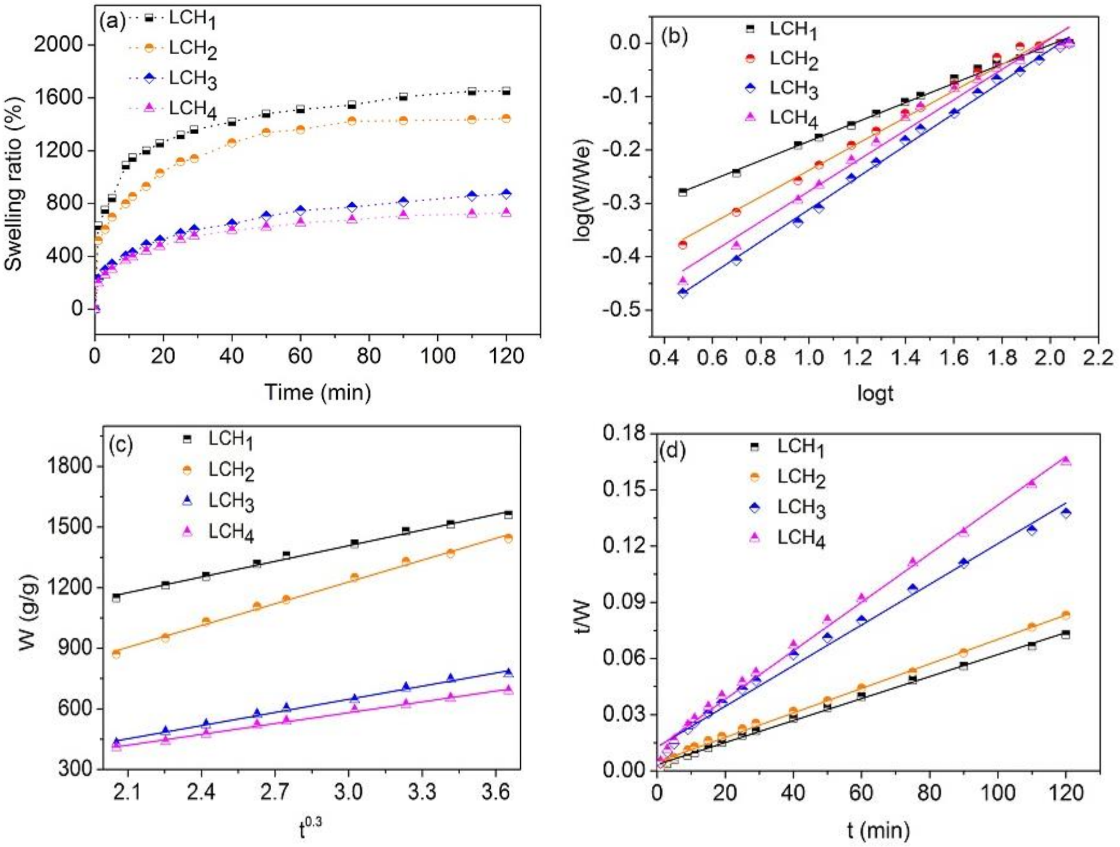

Fig. 5. Swelling behaviors of LCH_{1-4}. (a) Swelling rates of hydrogels in deionized water at 25 ^{o}C; (b) plots of log(W/W_e) against log t for the hydrogels; (c) fitting results for the Fickian model; (d) fitting results for the Schott model

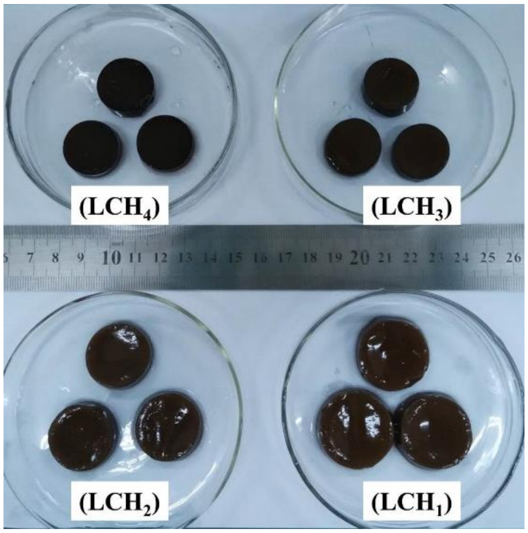

Fig. 6. The photographs of LCH_{1-4}

According to the exponential heuristic equation, one plot is made with lg(W/W_e) as the ordinate and lg$t$ as the abscissa, as shown in Fig. 5. The values of n and K can be calculated from the slope and intercepts of the lines (Table 3). In Table 3, the value of n for LCHs is approximately 0.3, which indicates that the diffusion rate for water penetrating into the composite hydrogels is low and is diffusion-controlled (Fickian diffusion).

The swelling kinetics were studied using Fickian and Schott models, respectively (Schott 1992). A pre-condition for the application of Fickian law is that the diffusion coefficient does not remain constant. Therefore, the swelling kinetics of the hydrogels as determined by the Fickian model are in the time range of 5 and 65 min, as shown in Fig. 5. The corresponding parameters are listed in Table 3. It is obvious that a linear relationship between W and $t^{0.3}$ is obtained, and the correlation coefficient r^2 values approached or exceeded 0.99, which indicates that the initial swelling process displays Fickian behavior.

The Schott model, which was used to investigate the process of swelling, has a linear form that can be expressed as follows:

$$\frac{\mathrm{t}}{W}=\frac{1}{KW_e^{2}}+\frac{\mathrm{t}}{W_e} \tag{5}$$

in which W is the swelling ratio of the hydrogel at a given time t, W_e is the swelling ratio of the hydrogel at equilibrium, and K is the rate constant. The values of W_e and K are evaluated by the slope and intercept of the plot. Figure 5a shows the swelling kinetics of the hydrogels as evaluated by the Schott model, whose correlation coefficients are listed in Table 3. The r^2 values for all the hydrogels were approximately 0.99, so the experimental data were well-fitted by the Schott model. The value of the experimental swelling capacity of water ($W_{e,exp}$) is very near the value from the Schott model ($W_{e,exp}$).

Table 3. Thermal Fickian Model and Schott Model Correlation Coefficients

Samples ID	Fickian model				Schott model			
	n	K	r^2		K	$W_{e,cal}$ (g·g^{-1})	$W_{e,exp}$ (g·g^{-1})	r^2
LCH$_1$	0.2805	0.4326	0.9961		1.017e-4	1703.34	1650.66	0.9976
LCH$_2$	0.2477	0.3268	0.9877		8.971e-5	1528.68	1443.98	0.9969
LCH$_3$	0.2994	0.2450	0.9965		1.090e-3	917.43	872.35	0.9887
LCH$_4$	0.2852	0.2740	0.9832		1.375e-4	769.23	722.31	0.9952

CONCLUSIONS

1. Lignin-containing hydrogels were successfully synthesized and characterized using [Emim]Ac as the solvent.
2. The swelling behaviors of LCHs were noticeably influenced by the content of lignin, in which the highest swelling degree (1,650%) was obtained with 6.25 wt% lignin.
3. The kinetics study revealed that the swelling behaviors of LCHs were well-fitted by the Schott model.

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