Hardwood Kraft Lignin-Based Hydrogels: Production and Performance

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ABSTRACT: In this study, hydrogels were synthesized through the radical polymerization of hardwood kraft lignin, N-isopropylacrylamide, and N,N'-methylenebisacrylamide. Statistical analyses were employed to produce lignin-based hydrogels with the highest yield and swelling capacity. The success of the polymerization reactions was confirmed by NMR and Fourier infrared spectroscopy. The lignin-based hydrogel was more thermally and rheological stable, but exhibited less swelling affinity, than synthetic hydrogel. The rheological studies indicated that the swollen hydrogels were predominantly elastic and exhibited a critical solution temperature that was between 34 and 37 °C. Compared with the synthetic hydrogel, lignin-based hydrogel behaved less elastic as temperature increased. In addition to inducing a green hydrogel, the results confirmed that hardwood lignin-based hydrogel would have different properties than synthetic-based hydrogels, which could be beneficial for some applications.

INTRODUCTION

Hydrogels are often described as three-dimensional polymeric networks formed from cross-linked hydrophilic homopolymers, copolymers, or macromers.1−4 They are insoluble polymer matrices capable of retaining a large amount of water in their swollen state; in some cases, up to a thousand times of their dry weight. Their swelling capability allows them to obtain the shape of their surroundings when confined.5−6

Depending on the source of polymers, hydrogels may be synthetic, natural, or hybrid.5 Hydrogels may be degradable in aqueous environments, making them biocompatible in most cases and a good carrier for nutrients to cells and their metabolic products.5 They have been deemed to be efficient in the protection of cells and fragile drugs, such as peptides and proteins.5 Some hydrogels have exhibited stimuli-induced swelling and deswelling capabilities without disintegration.7−9

The advantage of tunable properties has given hydrogels attention for biomedical and environmental applications.10,11 Poly (N-isopropylacrylamide) (PNIPAAm) is a thermoresponsive hydrogel.12−14 However, the applications of PNIPAAm hydrogels are limited by their fragility.15,16 These applications can be extended via enhancing their rigidity.17−20

Recently, lignin (LGN) has been incorporated into the production of flocculants, dispersants, and hydrogels because lignin is biocompatible and biodegradable with low toxicity.17−20 At a relatively low production cost,21 lignin presents the greatest available aromatic renewable resource worldwide, as well as a primary supplier of soil’s organic matter.2,6,22 Lignin provides the structural strength of plants by nature, which makes it a potential candidate for PNIPAAm hydrogel modifications.

Previous studies have been conducted on synthesizing hydrogels using different types of lignin through free radical polymerization. Acetic acid lignin was incorporated into N-isopropylacrylamide (NIPAAm) for hydrogel production.23 The kinetics studies indicated that the lignin-containing hydrogel retained 7.2% more water than the lignin-free hydrogel over 10 min of swelling.23 In another work, wheat straw alkali lignin was cross-linked with acrylic acid and N,N'-methylenebisacrylamide (MBAAm) via free radical polymerization.24 The addition of acid hydrolysis lignin was found to greatly improve the surface morphology and swelling affinity of the hydrogel.25 Yu et al. developed lignosulfonate-g-acrylic acid hydrogels by grafting acrylic acid onto lignosulfonate with MBAAm as a cross-linker and lacase/tert-butyl hydroperoxide as the initiator.26

It is well known that the type of lignin (i.e., hardwood vs softwood vs nonwood) and its production process (i.e., enzymatic hydrolysis vs kraft vs sulfite treatment) affect its structure and chemical properties, which, in turn, affect its polymerization performance and end-use applications.27−32 There is currently limited research on the use of hardwood kraft lignin for hydrogel production following free radical polymerization. As hardwood is vastly available for end-use polymerization performance and end-use applications, it is of great importance to investigate the performance of hardwood lignin for hydrogel productions.17−21

The first objective of this study was to evaluate the cross-linking of hardwood-based kraft lignin with NIPAAm as the...
monomer and MBAAm as the cross-linker. The second objective of this study was to investigate the thermal and rheological properties of kraft lignin-based hydrogels, as well as their swelling performance. The main novelty of this work was...
The investigations on the use of hardwood kraft lignin as a commercially available resource in hydrogel production and on the properties and performance of the induced hydrogels under different scenarios.

## RESULTS AND DISCUSSION

**Polymerization.** The free radical polymerization for producing lignin-based hydrogels is demonstrated in Figure 1. Azobisisobutyronitrile (AIBN) first undergoes thermal decomposition to generate radicals, which initiates the polymerization. Figure 1a demonstrates the thermal decomposition of the azo compounds with heating, which produces two 2-cyanoprop-2-yl radicals and nitrogen gas. In this case, 2-cyanoprop-2-yl radicals can then be transferred to lignin, NIPAAm, or MBAm present in the reaction mixture. When the free radical is transferred to lignin, it will abstract hydrogen from the hydroxyl group located on lignin’s aromatic ring generating a phenoxy radical (I in Figure 1b) along with the corresponding resonance structures (II in Figure 1b). The phenoxy radicals will then attack the carbon double bonds of the NIPAAm monomers and the cross-linker MBAm to form the cross-linked structure (Figure 1c). The radical polymerization is most commonly terminated through the reactions but to change the quantity of other components of the reaction. The range of analysis was optimized by evaluating the signal-to-noise (SN) ratio to maximize the responses of the model. The hydrogel sample of 2L was selected as the best hydrogel sample based on the results achieved. The control sample (2C) was produced following reaction conditions of 2L but without lignin.

Multivariate analysis (MANOVA) was applied to determine whether there are differences among the levels and factors. A 95% confidence interval was selected, implying that the response is deemed significant if the P-value is smaller than 0.05. Furthermore, post hoc analysis was applied to determine where these significant differences exist when considering multiple levels. Tukey’s test was selected as an effective post hoc model to compare all the possible pairs of means and determine where they differ within the data.

Table 2 demonstrates the results of the MANOVA for the responses of lignin-based hydrogels. It is observable that temperature presents a significant effect on yield (F = 7.84, p = 0.011, η² = 0.635) and maximum swelling ratio (F = 14.07, p = 0.002, η² = 0.076). The cleavage of the azo compounds may occur more rapidly at higher temperatures, increasing the concentration of radicals present in the solution and facilitating the reaction. This table also shows that the reaction time presents a large effect with respect to yield (F = 222.24, p < 0.001, η² = 0.980). This is because the time extension allows for additional cross-linking to occur in the reaction, resulting in products in reactions. Compared with other reactants in this polymerization reaction system, lignin is more difficult to handle in terms of its solubility, reactivity, and pH adjustment in solutions. Therefore, to have a better control over the reactions, we decided to keep the amount of lignin constant in the reactions but to change the quantity of other components of the reaction. The range of analysis was optimized by evaluating the signal-to-noise (SN) ratio to maximize the responses of the model. The hydrogel sample of 2L was selected as the best hydrogel sample based on the results achieved. The control sample (2C) was produced following reaction conditions of 2L but without lignin.

Table 2. Multivariate Analysis of the Taguchi L9 Orthogonal Model for the Lignin-Based Hydrogels

| source                | dependent variable | sum of squares | degrees of freedom | mean square | F-value | P-value | η² | observed power |
|-----------------------|--------------------|----------------|--------------------|-------------|---------|---------|----|----------------|
| model                 | yield              | 2852.78        | 8                  | 356.60      | 80.10   | 0.000   | 0.986 | 1.000          |
|                       | swelling ratio     | 777.82         | 8                  | 97.23       | 20.53   | 0.000   | 0.948 | 1.000          |
| temperature (°C)      | yield              | 69.07          | 2                  | 34.54       | 7.84    | 0.011   | 0.635 | 0.852          |
|                       | swelling ratio     | 133.27         | 2                  | 66.63       | 14.07   | 0.002   | 0.758 | 0.983          |
| time (h)              | yield              | 1956.94        | 2                  | 978.47      | 222.24  | 0.000   | 0.980 | 1.000          |
|                       | swelling ratio     | 183.67         | 2                  | 91.83       | 19.39   | 0.001   | 0.812 | 0.998          |
| NIPAAm content (g)    | yield              | 378.66         | 2                  | 189.33      | 43.00   | 0.000   | 0.905 | 1.000          |
|                       | swelling ratio     | 157.85         | 2                  | 78.92       | 16.67   | 0.001   | 0.787 | 0.993          |
| pH                    | yield              | 448.11         | 2                  | 224.05      | 50.89   | 0.000   | 0.919 | 1.000          |
|                       | swelling ratio     | 303.03         | 2                  | 151.52      | 32.00   | 0.000   | 0.877 | 1.000          |
| pure error            | yield              | 39.62          | 9                  | 4.40        |         |         |      |                |
|                       | swelling ratio     | 42.61          | 9                  | 4.73        |         |         |      |                |
| corrected total       | yield              | 2892.41        | 17                 |             | 162.05  | 0.000   |      |                |
|                       | swelling ratio     | 820.43         | 17                 |             |         |         |      |                |
a higher product yield. A significantly large decrease in yield \((F = 43.00, p < 0.001, \eta^2 = 0.905)\) and swelling capacity \((F = 16.67, p = 0.001, \eta^2 = 0.787)\) with increasing NIPAAm content was determined between 18 and 24 g/g of lignin. The higher incorporation of monomer into the hydrogels was found to improve the hydrogel production. Furthermore, the yield \((F = 50.89, p < 0.001, \eta^2 = 0.919)\) and the maximum swelling ratio \((F = 32.00, p < 0.001, \eta^2 = 0.877)\) exhibit a significant effect between pH 2.0 and pH 2.5.

Table 3 compares the means and standard deviations for both responses, as well as the associated coefficients. The responses exhibited a low coefficient of variation, implying that the obtained data are considered as precise and repeatable.41

To determine which lignin-based hydrogel sample exhibited the best responses, the signal-to-noise (SN) ratio was determined in the Taguchi analysis. Because the goal for this experiment was to maximize the response values, the larger-the-better (LB) SN ratio equation, eq 1, was selected42

\[
S/N_{LB} = -10 \log \left( \frac{1}{n} \sum_{i=1}^{n} \frac{1}{y_i} \right)
\]  

(1)

where \(n\) is the number of experiments and \(y_i\) is the collected experimental data. The optimal level can then be determined by selecting the largest SN ratio from each of the performance parameters.42 Table 1 lists the signal to noise ratios for selected lignin-based hydrogel samples, along with their responses (yield and maximum swelling ratio). The SN values, which maximized both of these responses, were found to be the highest for 2L. Thus, this sample was selected as the optimum sample based on the results.

### NMR Evaluation

Figure 2 illustrates the \(^1\text{H} \text{NMR}\) spectrum for the lignin-based hydrogels. The peak at 1.15 ppm corresponds to two methyl protons of the \(N\)-isopropyl group (A). The proton of the \(N\)-isopropyl group (E) is present at 4.1 ppm. These large peaks are dominant over the others due to the large content of NIPAAm within the hydrogels.43,44 The functional groups for lignin are depicted by a cluster of small peaks from 5 to 8 ppm, which may be due to the aromatic rings present in kraft lignin. The peak of dimethyl sulfoxide (DMSO) is observable at 2.6 ppm, which belongs to dimethyl sulfoxide, DMSO, (D).43

### Fourier Transform Infrared Spectroscopy (FTIR) Evaluation

The FTIR spectra of the selected hydrogels with lignin, 2L, and without lignin, 2C, are shown in Figure 3. The bands located between 1535 and 1639 cm\(^{-1}\) are attributed to the amide groups found in NIPAAm as well as in \(N,N'\)-methylenebisacrylamide.45,46 These compounds also exhibit a broad spectrum between 3400 and 3200 cm\(^{-1}\), indicating the stretching of the \(N-H\) bond.45,47,48 According to Konduri and Fatehi,49 the presence of kraft lignin’s aromatic compounds yields a broad peak between 1593 and 1510 cm\(^{-1}\), which is attributed to the benzene ring vibrations. There are also absorption peaks present at 1130 and 1171 cm\(^{-1}\), which correspond to the stretching of the C=O bond on the primary alcohol and ether of kraft lignin, respectively.45 In addition, the C=O and C=C stretching may be depicted by the bands

**Table 3. Descriptive Statistics**

| dependent variable | standard deviation | mean | 95% confidence interval | lower bound | upper bound | coefficient of variation (%) |
|--------------------|--------------------|------|-------------------------|-------------|-------------|-----------------------------|
| yield              | 2.10               | 77.77| 76.65                   | 78.89       | 2.70        |                             |
| swelling ratio     | 2.18               | 22.48| 21.32                   | 23.64       | 9.68        |                             |

Figure 2. \(^1\text{H} \text{NMR}\) spectrum for lignin-based hydrogels (sample 2L).
located at approximately 1200 and 1500 cm\(^{-1}\), respectively. The CH stretching of methyl or methylene groups are also shown to be present in the peaks between 2300 and 2400 cm\(^{-1}\). The peaks at 1535 and 1639 cm\(^{-1}\) were intense for both samples, indicating the presence of NIPAAm. For this reason, the peaks for NIPAAm overshadow the peaks at 1593 and 1510 cm\(^{-1}\) for aromatic structure of lignin.

**TGA Evaluation.** The thermal decomposition behavior of hydrogels of 2L and 2C are shown in Figure 4. An initial weight loss of 10% is generally due to moisture removal. Afterward, lignin demonstrates a higher thermal stability in comparison with the other samples, a desirable property for additional end-use applications.\(^{49}\) Above 200 °C, lignin exhibits a gradual decrease in weight loss and levels off at a 55% weight loss above 600 °C. This is because the thermal breakdown of lignin occurs via two competing reaction paths of the intramolecular condensation and the thermal depolymerization.\(^{50-52}\)

Despite relatively similar trends, sample 2C is shown to be slightly less thermally stable than 2L. Sample 2C was found to exhibit a major weight loss at approximately 415 °C, whereas sample 2L exhibited a primary weight loss at around 420 °C. Zarzyka and co-workers described that the use of \(N, N'\)-methylenebiscrylamide allows for a higher cross-linking density, which, in turn, decreases the chain mobility within the gels.\(^{53}\) Because \(N, N'\)-methylenebiscrylamide contributes to cross-linking, it can be assumed that it was readily consumed during the thermal decomposition reaction.

**Surface Properties and Swelling Behavior.** The surface area properties of the selected samples are shown in Table 4. The hydrogel without lignin, 2C, was found to have a higher surface area, pore volume, and pore size compared to the lignin-based hydrogel, 2L. This indicates that 2C hydrogel has a more porous structure.\(^{23}\) Lignin-based hydrogel is expected to become less hydrophilic than its synthetic form due to the incorporation of a hydrophobic polymer (lignin). Therefore, this hydrogel (2C) exhibited a better swelling performance in water, as presumably water molecules could diffuse into its pores more effectively.

Previous studies showed that the swelling performance of lignin hydrogels varied in a wide range depending on the hydrogel components (e.g., lignin types and monomers).\(^{25}\) For example, lignin-based poly(acrylic acid) (PAA) hydrogels showed relatively high swelling ratios of 400, 600, and 700 g/g for acid hydrolysis lignin–PAA, alkali lignin–PAA, and lignosulfonate–PAA hydrogels, respectively.\(^{24,25}\) The specific surface area of alkali lignin–PAA hydrogel was reported to be as high as 122.7 ± 4.51 m\(^2\)/g.\(^{24}\) On the other hand, hydrogels synthesized by acrylamide and poly(vinyl alcohol) with

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**Figure 3.** FTIR analysis for hydrogels with lignin, 2L, and without lignin, 2C.

**Figure 4.** Weight loss and weight loss rates of control and lignin-based hydrogels: (a) kraft lignin, (b) 2C, and (c) 2L.

**Table 4. Surface and Swelling Properties of Hydrogels**

| sample | surface area (m\(^2\)/g) | total pore volume (cm\(^3\)/g) | average pore size (Å) | maximum swelling ratio (g/g) |
|--------|---------------------------|-------------------------------|-----------------------|-------------------------------|
| 2C     | 49.62                     | 0.058                         | 24.9                  | 36.22                         |
| 2L     | 44.56                     | 0.048                         | 22.1                  | 32.59                         |
alkaline and kraft lignin had a swelling ratio of 8 and 1.5 g/g, respectively.\textsuperscript{29,52} When cross-linking with NIPAAm, the hardwood kraft lignin-based hydrogel obtained in this study exhibited a much higher swelling ratio compared to the acetic acid lignin-based hydrogel.\textsuperscript{23}

**Rheological Behavior.** The cross-linked structure of hydrogels can be further characterized by applying dynamic oscillatory experiment. A sinusoidal oscillation with a given deformation and frequency can be applied onto a material to obtain sinusoidal output for strain.\textsuperscript{53} Their viscoelastic properties may be characterized by storage modulus ($G'$), which describes the material’s elasticity, and loss modulus ($G''$), which is attributed to the viscosity of materials. The elastic component characterizes a material’s solid-like ability to store energy (its stiffness), whereas the viscous component is the liquid-like capability to dissipate energy.\textsuperscript{54,55}

Figure 5 illustrates the effect of frequency on storage ($G'$) and loss ($G''$) modulus as well as on dynamic viscosity ($\eta$) for both the control and lignin-based hydrogel samples. Some loss modulus values were unable to be measured accurately at low frequencies and are thus analyzed from 6.30 rad/s for both samples.\textsuperscript{56} The storage modulus is greater than that of the loss modulus for both cases (Figure 5), indicating that the hydrogel samples exhibit more elastic properties. This behavior is typical for hydrogels as the solid-like mechanical properties of their cross-linked structure are more dominant than the viscous properties, which is attributed to the small amorphous part of the polymer network.\textsuperscript{53}

In addition, both storage and loss modulus were found to increase with increasing shear frequency, allowing for more energy to be dissipated. Although frequency is shown to influence the moduli curves, its dependence is largely insignificant, indicating that the hydrogels have a well-structured three-dimensional network.\textsuperscript{57} Furthermore, the dynamic viscosity is shown to linearly decrease with increasing frequency, an attribute typical to hydrogels.\textsuperscript{53} The amount of energy dissipated was found to be slightly greater for the control samples (2C) than for the lignin-based sample (2L). This may be due to the incorporation of lignin resulting in a less cross-linked structure. In other words, the network structure of the control samples is more tightly cross-linked and is therefore better able to dissipate energy.

For amplitude sweep test, linear viscoelastic region (LVR) for both samples are shown in Figure 6. The strain applied does not exhibit a strong effect on the moduli, which serves as an indication of the hydrogels’ rigidity.\textsuperscript{58} In addition, the storage modulus is shown to exhibit a greater plateau, indicating that the samples’ viscoelastic behavior.\textsuperscript{59}

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**Figure 5.** Frequency sweep of the control and lignin-based hydrogels: (a) moduli of 2C and 2L and (b) dynamic viscosity of 2C and 2L.

**Figure 6.** Strain amplitude sweep of the control and lignin-based hydrogels: (a) 2C and (b) 2L.
On the other hand, the storage modulus is shown to significantly decrease with increasing strain, indicating a disturbance within the network structure. The loss modulus slightly increases before rapidly decreasing to 100% strain. This maximum indicates the microscopic failure within the hydrogel’s network structure, which indicates breaking of the interaction present within the polymer matrix. At this point, the storage and loss moduli exhibit a crossover where the hydrogel exhibits a phase change from primarily elastic to primarily viscous. This indicates the irreversible deformation of the three-dimensional network structure, which provides the hydrogel its elasticity.

The crossover for the hydrogel 2C was shown to occur at a lower strain rate compared to the hydrogel 2L. This increase in rheological stability with applied strain is most likely due to the incorporation of lignin. In addition, the LVR has a larger width for the lignin-based sample compared with the control sample, further supporting that the incorporation of lignin increases the samples’ rigidity.

Figure 7 shows the effect of the stress on the modulus resulting from amplitude sweep tests. The initial plateau designates the LVR, for which the change in modulus is denoted by the yield point ($\tau_y$). As the modulus exhibits a crossover from mainly elastic to mainly viscoelastic, this crossover is known as the flow point ($\tau_f$). These results for both these points are summarized in Table 5. The flow point and yield point for the lignin-based hydrogel were found to be greater than those for the control sample, indicating that lignin improved the hydrogels’ rheological performance.

| sample | yield point, $\tau_y$ (Pa) | flow point, $\tau_f$ (Pa) |
|--------|--------------------------|--------------------------|
| 2C     | 95.1                     | 175.2                    |
| 2L     | 216.1                    | 628.9                    |

Figure 8 demonstrates the rheological properties for both elastic and viscous moduli of the hydrogel samples at different temperatures. At low temperatures, the moduli curves dropped with increasing temperature. At approximately 34–37 °C, there is a slight valley in the moduli curves, which is attributed to the lower critical solution temperature (LCST) of NIPAAm (32–34 °C). At this temperature, the hydrogels undergo a reversible phase transition from their swollen state to a shrunken dehydrated state. Afterward, the difference between the elastic and viscous moduli becomes smaller, but does not reach a crossover temperature. In other words, the hydrogel samples do not exhibit a phase transition, but rather undergo a plateau with increasing temperature, indicating their thermal stability.

The control hydrogel (2C) exhibits a larger modulus than the lignin-based hydrogel (2L), indicating that the control hydrogel has more elastic properties even with increasing temperature. In addition, following the LCST, the gap between the elastic and viscous modulus decreases more significantly for the lignin-based hydrogels, which suggests that the lignin-
based hydrogels approach the sol–gel temperature more readily than the control hydrogel.62

■ CONCLUSIONS

Hardwood lignin-based hydrogels were successfully produced through radical polymerization of lignin, NIPAAm, and MBAAm, as confirmed by the NMR and FTIR analyses. Thermogravimetric analysis determined that the hydrogels exhibited two decomposition stages attributed to the breakdown of the aliphatic alkenes groups and the remaining carboxylic and amine groups. Although lignin-based hydrogel had less swelling affinity, as it possessed smaller surface area and more porous structure than synthetic one, it was more thermally stable. The slightly greater energy dissipated for the control hydrogel than for the lignin-based hydrogel implied that the incorporation of lignin generated less cross-linked hydrogel. Lignin tended to increase the rigidity and rheological stability of hydrogel. Compared with the control hydrogel, lignin-based hydrogel behaved less elastic as temperature increased. These results suggest that hardwood lignin-based hydrogel can be produced, but its properties are different from synthetic-based hydrogels.

■ METHODOLOGY

Materials. Mixed hardwood kraft lignin (LGN) was supplied by FPInnovations’ pilot plant facility located in Thunder Bay, ON. NIPAAm (97%), MBAAm (99%), azobisisobutyronitrile (AIBN, 98%), acetone (97%), dimethyl sulfoxide-δ6 (DMSO, 99.9% atom D), and tetramethylthionine chloride (methylene blue) were obtained from Sigma-Aldrich. Sulfuric acid (98%) and sodium hydroxide (97%) were also obtained from Sigma-Aldrich and diluted with deionized water. Thunder Bay, ON. NIPAAm (97%), MBAAm (99%)

Sulfuric acid (98%) and sodium hydroxide (97%) were also obtained from Sigma-Aldrich. Sulfuric acid (98%) and sodium hydroxide (97%) were also obtained from Sigma-Aldrich and diluted with deionized water.

Reaction. In this set of experiments, 0.1 g of kraft lignin, 0.06 g of MBAAm, and varying concentrations of NIPAAm (1.2–2.4 g) were dissolved in round-bottom glass flasks with deionized distilled water. The pH of the solutions was then adjusted with 20% sulfuric acid and 10% sodium hydroxide to pH 2.0–3.0 before being purging with nitrogen gas for 30 min. Water was added into the flasks to generate the total mass of reaction (40 g), which includes the weight of the reactants. The flask was placed in a water bath and heated to the desired temperature before adding 0.08 g of the AIBN initiator. The reaction was then allowed to proceed at the steady-state temperature (65–85 °C), with a constant flow of nitrogen gas at 220 rpm. This procedure was repeated for samples with and without lignin. After completion, the hydrogel samples were extracted from the flasks and rinsed with acetone to remove unreacted monomers. The hydrogels were then rinsed with water to prevent further degradation and freeze-dried at −50 °C for over 24 h in a Labconco FreeZone 1L freeze-dryer. The yield of the hydrogel production was calculated following eq 2

\[
yield(%) = \frac{W_{\text{hydrogel}}}{W_{\text{LGN}} + W_{\text{NIPAAm}} + W_{\text{MBAAm}} + W_{\text{AIBN}}} \times 100\%
\]

where \(W_{\text{hydrogel}}\) is the total dry weight of the hydrogel (g) and \(W_{\text{LGN}}, W_{\text{NIPAAm}}, W_{\text{MBAAm}}, W_{\text{AIBN}}\) are the initial weights of lignin, NIPAAm, MBAAm, and AIBN, respectively.

The L9 Taguchi orthogonal design was performed with four factors (each containing three levels) to investigate the effect of reaction parameters on the responses (i.e., yield of reaction and swelling ratio) for producing hydrogels.

\[ ^1H \text{NMR Spectroscopy.} \] The freeze-dried hydrogel samples were ground to powder before being dissolved in 0.5 g of deuterated dimethyl sulfoxide (DMSO-δ6), and placed into a 5 mm, 500 MHz glass NMR tube. The sample containing tubes were inserted into the Varian Unity INOVA 500 MHz NMR machine. The \(^1H\) NMR spectra of the samples were acquired at a 15° pulse flipping angle, a 4.6 μs pulse width, a 2.05 acquisition time, and 1 s relaxation delay time.

\[ \text{Fourier Transform Infrared Spectroscopy.} \] Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted for the selected hydrogel samples (0.001 g) using a Bruker Tensor 37 (Germany, ATR accessory). The IR spectra was recorded in transmittance mode within the wave number range of 500–4000 cm\(^{-1}\) with a 4 cm\(^{-1}\) resolution.

\[ \text{Brunauer–Emmett–Teller (BET) Surface Analysis.} \] The surface area of the hydrogel particles was determined by using a Quantachrome surface area analyzer, Nova 2200e, instrument. The freeze-dried hydrogels were first ground to powder and passed through multiple sieves. The particles with the size fraction between 150 and 300 μm were selected for analysis. For each test, 0.05 g of the powder samples were taken into account for specific surface area analysis according to Brunauer–Emmett–Teller (BET) method via adsorption–desorption isotherms using nitrogen gas at −180 °C with the relative pressure range of 0.01–0.99.

\[ \text{Thermogravimetric Analysis (TGA).} \] The dried powder hydrogel samples were placed in a desiccator overnight before undergoing thermal analysis using a thermogravimetric analyzer (TGA i-1000 series, Instrument Specialist Inc.). Approximately, 8 mg of sample was heated at a constant flow rate of nitrogen (35 mL/min) from room temperature to 700 °C at the heating rate of 10 °C/min.

\[ \text{Swelling Performance.} \] The freeze-dried hydrogel samples were cut and divided into samples weighing approximately 0.2 g. The dried samples (with a known weight) were immersed into 200 mL of deionized water for 24 h. The swelling ratio was determined by considering the swollen weight of the hydrogel samples and the initial weight of dried hydrogels following eq 3

\[
Q = \frac{W_{\text{swollen}} - W_{\text{dry}}}{W_{\text{dry}}}
\]

where \(W_{\text{swollen}}\) is the weight of the swollen hydrogel and \(W_{\text{dry}}\) is the initial weight of the dry hydrogel.

\[ \text{Rheology.} \] A rheometer, TA Instruments, Discovery HR-2, with a Peltier temperature control system was used for analyzing the viscoelastic properties of hydrogel samples. The upper geometry was a 40 mm steel parallel plate with a gap of 1 mm and a loading gap of 60 mm. The dynamic oscillatory measurements were carried out at a constant temperature of 25 °C, unless stated otherwise. The hydrogels were prepared for the rheology test according to the method described elsewhere.53 The hydrogel samples were saturated in deionized water before testing and were loaded onto the Peltier plate to cover the surface area of the parallel plate. Attempts have been made so that the same amount of the hydrogel samples with similar thickness was loaded on the Peltier plate for each test. Three tests of frequency sweep, amplitude sweep, and temperature ramp have been applied on the samples in this set of experiments. The frequency test was carried out at a relative pressure range of 0.01–0.99.
shear stress of 0.2 Pa throughout the frequency range of 0.2–
20 Hz (1.267–125.7 rad/s). The amplitude sweep was obtained at a constant frequency mode of 10 rad/s over a strain rate range of 0.01–1000%. The temperature ramp was recorded at a constant strain rate of 2%, with a low frequency of 10 rad/s over a temperature range of 0–50 °C. The temperature ramp rate was 5 °C/min.

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**Notes**

The authors declare no competing financial interest.

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