Influence of Temperature and pH Conditions on the Swelling Properties of Rice Straw Derived Cellulose Hydrogel

Vu Tung Lam, Nguyen Ngoc Mai[*]
Hanoi University of Science and Technology, Hanoi, Vietnam
[*]Corresponding author email: mai.nguyenngoc@hust.edu.vn

Abstract

Cellulose, one of the renewable and biodegradable polymers, has been extensively studied as a raw material for a newly and fully bio-based hydrogel. The synthesis of bio-hydrogel is based on the dissolution of extracted cellulose from rice straw in tetrabutylphosphonium hydroxide (TBPH) solvent followed by the gelation using epichlorohydrin (ECH) crosslinkers. The success of the extraction of cellulose from rice straw was evaluated by characteristic peaks of cellulose in Fourier Transform Infrared Spectroscopy (FTIR) spectrum. The hydrogel formation mechanism was investigated in this article, as well as the evaluation of swelling properties under different temperature and pH conditions. As hydrogel exhibited thermal and pH sensitive behavior, the highest swelling capacity was found at pH 7.0 and 60 °C. The characterization of hydrogel was examined by Fourier Transform Infrared Spectroscopy (FTIR) and thermal analysis (TGA), indicating that the rice straw derived cellulose hydrogel was cellulose type II, similar to others hydrogels. The morphology of extracted cellulose and hydrogel were investigated by Scanning Electron Microscope (SEM). The hydrogel exhibited porosity structure with very large pore size that surrounded by cellulose/ECH layers. The purity of the hydrogel was determined through the amount of water immersed in the hydrogel for one day by Liquid Nuclear Magnetic Resonance (NMR) for the residual TBPH determination.

Keywords: Cellulose hydrogel, cellulose extraction, rice straw, swelling properties, tetrabutylphosphonium hydroxide

1. Introduction

Over recent years, biomass resources have been impressive materials in hydrogels fabrications due to their biodegradability, biocompatibility, and biological properties [1]. The main biomass resources in Vietnam are agricultural waste from wheat, rice, and sugar cane crop residues. It is estimated that nearly 60-90 million tons of rice straw are generated annually. However, the treatment for these residues at the moment is burning directly, which is not only harmful to the environment and human health but also ignores its potential as a cheap and clean natural resource. Moreover, rice straw is a huge source of organic matter, accounting for up to 80 % of the weight of the rice plant; each hectare of rice cultivation contains 10 to 12 tons of straw [2]. Therefore, it is urgent to avoid burning rice straw and use it as a valuable source.

Extracting from rice straw, the primary components are cellulose, hemicelluloses, lignin, and other compounds, in which cellulose is playing a vital role in creating paper products, fibers, pharmaceuticals, or creating materials [3]. Cellulose is considered an alternative material owing to its environmental friendly, cost-effective, and biodegradable; therefore, being applied in polymer industry, cotton, dye, nanotechnology, and hydrogels.

The environmental friendly utilisation of cellulose constitutes a very important topic towards the use of renewable raw materials. The common solvents to dissolve cellulose are lithium chloride/dimethylacetamide (LiCl/DMAc), N-methylmorpholine-N-oxide (NMMO), and ionic liquids (ILs) [3]. Most of the current solvents have undesirable properties such as high toxicity, thermal instability, volatility, and high cost, which has triggered the search for alternative, more environmentally friendly substitutes with greater sustainability implications. Although some polar ILs are recognized as effective solvents for cellulose, they still have a serious problem because the addition of water significantly reduces the solubility of cellulose in the ILs. It is therefore of great importance to develop alternative solvents that can dissolve cellulose at room temperature even in the presence of water. In this study, electrolyte solution of tetrabutylphosphonium hydroxide (TBPH) in water can dissolve easily cellulose or biomass at room temperature [4]. Furthermore, TBPH can dissolve a much higher amount of cellulose than that of an alkali/urea solution (with a maximum solubility of 3 wt.%) and an ionic liquid (1-ethyl -3-methyl imidazolium acetate (EMIM Acetate) (5-10 wt.%), which can occur even at room temperature [4].

In cellulose applications, cellulose has been extensively explored as a raw material for a new and fully bio-based hydrogel. Hydrogels have been classified variously throughout history. From first generation hydrogels with good mechanical and swelling properties, to second generation stimuli-responsive hydrogels, to third generation hydrogels consisting of complexing materials. Hydrogels can be synthesized from monomers such as vinyl or acrylic and a free-radical initiator compound [5]. However, more environmentally friendly hydrogels are required for pharmaceuticals and medicine, and cellulose-based hydrogels have already attracted the attention of scientists in the first generation because they are used as a matrix for drug dispersion [6]. On the other hand, cellulosic hydrogel is known for its adaptability, bio-materials, and can be synthesized under normal conditions. There have been various research surrounding the use of different crosslinking agents to produce cellulose derivative hydrogels [6]. For crosslinkers, it is required to have a hydrophilic properties to be able to make crosslinking with other materials [7]. That article concluded that various methods, such as freeze-thawing to create physical crosslinking or chemical crosslinking has been studied. Physical crosslinking method is much more easier owing to lesser number of intermediate steps [7]. However, the method does not always deliver the desired material properties. For the chemical crosslinker agent, epichlorohydrin (ECH) was used for chemical crosslinking in hydrogel structure.

On account of its structure, the ability to uptake a large amount of water makes hydrogel really stand out in the biomedical field. It can be used to apply to wounds, regenerate tissue or as an agent for drug delivery inside the human body. That's why it is essential to study the behavior of hydrogels after it is ingested to the human body, with different factors to be considered, with different pH and conditions in different organs, precisely. In the research, our objective is two main influence factors in hydrogel's swelling ability, which are pH and temperature. These results provided valuable insights into the behavior of hydrogels in medical applications under different conditions. The characterization of hydrogel was investigated by Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR - FTIR) and thermal analysis (TGA). The morphology of extracted cellulose and hydrogel were investigated by Scanning Electron Microscope (SEM). The purity of the hydrogel was determined through the amount of water immersed in the hydrogel for one day by Liquid Nuclear Magnetic Resonance (NMR) for residual TBPH determination.

2. Materials and Methods

2.1. Materials

Tetrabutylphosphonium hydroxide (TBPH) containing 40 wt.% in water was purchased from Acros and concentrated through rotary evaporation under 70 bar, 40 °C to get a higher concentration (50 wt.% in water). Rice straw was harvested from a local farm in Thai Binh Province, Vietnam. It was cleaned of dirt and dried. Then, it was cut into small pieces of about 0.5 cm in length by a crusher. The chemical composition of rice straw can be characterized by five primary components: cellulose (32-33%), hemicellulose (19-20%), lignin (20-21%), extractable compound (4-6%) and ash (10-11%). Cellulose was extracted from rice straw by alkaline treatment with sodium hydroxide and ultrasound-assisted alkaline extraction [8]. The chemical agent (NaOH) was purchased from Merck Chemicals. Epichlorohydrin (ECH) was supplied from Sigma Aldrich.

2.2. Methods

2.2.1. Extraction cellulose from rice straw

Rice straw obtained from Thai Binh Province was cleaned of dirt and dried. Then, it was cut into small pieces of about 0.5 cm in length by a crusher. Cellulose is extracted from rice straw by alkaline treatment with sodium hydroxide NaOH and ultrasound-assisted alkaline extraction. The rice straw was first extracted with ultrasonic in alkaline medium (NaOH 2M) using TPC-280 Telsonic AG, (Switzerland, 20 kHz) for 30 min at high temperature 90 °C. The mixture was stirred at 400 rpm at 90 °C for 2 hours. Then, the mixture was washed with 0.1M NaOH to remove the residual lignin. After filtration, the cellulose-rich residue was washed again with distilled water and dried at 50 °C for 24 hours [8].

2.2.2. Dissolution cellulose in TBPH

The dissolution of cellulose is very important for further applications. Here an efficient and, nowadays more important, TBPH ([P_{4444}]OH, an organic base) which can be regarded as a significantly "greener" solvent system is used. Extracted cellulose (4 wt.% of cellulose) was dissolved in TBPH 50 wt.%. solution under stirring at 300 rpm for 1h at room temperature, forming a cellulose solution. After dissolution of cellulose in TBPH, a honey-like solution was obtained.
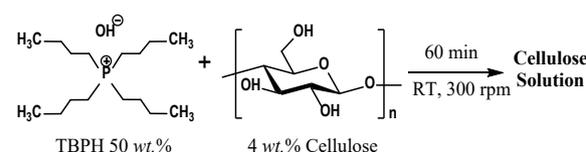
Fig. 1. Dissolution cellulose in TBPH 50 *wt.*%

2.2.3. Preparation of cellulose hydrogel

Cellulose hydrogels were synthesized by the following procedure in Fig. 2.
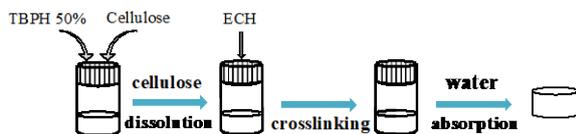
Fig. 2. Diagrammatic representation of the production process of cellulose hydrogel

A typical procedure involves the dissolution of 0.04 g cellulose in 1 ml TBPH 50 wt.% at room temperature (25 °C) followed by adding 0.06 ml ECH crosslinker. The crosslinker ratio between ECH:OH⁻ was 1:1. The gel solution was put into the molds to form the hydrogels at room temperature (25 ºC). Finally, the collected ion gels were washed with distilled water for about 23 hours to get hydrogels.

2.2.4. Evaluation of swelling behavior

To examine the adsorbed water capacity of hydrogel, the swelling degree (SD) was applied. The swelling degree was determined by the hydrogel's weight in a fully expanded state and in dry condition, both of which are measured at room temperature (25 °C). The swelling degree was calculated according to the equation:

$$SD = \frac{m_t - m_0}{m_0} \qquad (1)$$

where:

m_t is the mass of swollen hydrogel in gram at time t (minute)

m_0 is the mass of absolute dry hydrogel in gram

2.3. Characterizations of Cellulose Hydrogels

2.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra of samples were recorded on a Nicolet iS50 FTIR (Thermo Fisher Scientific) spectrometer in Attenuated total reflectance (ATR) mode. The specimens were measured directly with a scan range from 400 cm⁻¹ to 4000 cm⁻¹. The nominal instrument resolution was 4 cm⁻¹. Hydrogel sample was measured on a diamond built-in ATR window.

2.3.2. Nuclear Magnetic Resonance (NMR)

The samples were measured using deuterated solvents (D_2O) with a Bruker spectrometer AVANCE III 500 MHz at 125.8 MHz (2 s pulse delay, at room temperature 25 °C).

2.3.3. Thermal Analysis (TGA)

The thermogravimetric analysis (TGA) was carried out by using a STA 449F5 thermal analyzer (Netzsch). Amounts of about 5 mg of the carefully dried samples was sealed in aluminum oxide crucibles and investgated in the temperature range from 25 to 700 °C with heating rates of 10 °C min⁻¹ under inert atmosphere (50 ml min⁻¹ nitrogen).

2.3.4. Scanning Electron Microscope (SEM)

The hydrogel specimen was frozen using liquid nitrogen and freeze-dried under vacuum to obtain the structure inside. The morphologies of the freeze-dried cellulose hydrogel were investigated by scanning electron microscopy (Hitachi TM 4000 plus) at an accelerating voltage of 5kV. The morphology of extracted cellulose was recorded by scanning electron microscopy (Jeol NeoScope JCM7000 Benchtop) at an accelerating voltage of 5kV.

3. Results and Discussion

In order to modify cellulose efficiently, the cellulose requires dissolution. The solubility of cellulose has been studied for a long time but is constantly evolving. Abe *et al.* (2012) reported that tetrabutylphosphonium hydroxide (TBPH) have superior properties which can dissolve a large amount of cellulose (up to 20 wt.% cellulose) in a short time under mild conditions [4]. TBPH constitutes a non-toxic and recyclable solvent that can tolerate even large amounts of water and other standard solvents without losing dissolution capacity. To understand further the role of TBPH and ECH in the hydrogel formation, a mechanism is proposed (Fig. 3.). First, cellulose was dissolved and deprotonated in TBPH 50 wt.% at room temperature (25 ºC) result in the nucleophile OH⁻ of cellulose is formed. The obtained cellulose solution was then reacted with ECH by a SN2-type mechanism [9]. The nucleophile OH⁻ uses its lone pair electrons to attack the electrophilic carbon atom away from the departing halogen. This leads to a transition state with a partially formed C-OH bond and a partially broken C-Cl bond. When the C-OH bond forms fully and chloride ion departs with the electron pair from the former C-Cl bond, the product of ring opening was $NuCH_2CH(OH)CH_2Nu$ [9]. From this situation, the network structure of cellulose hydrogel was formed through the cross-linking reaction of free cellulose chains with ECH under basic condition.

It is worth noting that the intramolecular and intermolecular hydrogen bonds of cellulose form a hydrophobic site that contributes to its insolubility in water. As mentioned above, TBPH was chosen as the solvent because it has superior advantages over other solvents. During the dissolving step, the phosphonium cation of [TBP]⁺ and [OH]⁻ anion build hydrogen bonds between the hydroxyl groups of the cellulose structure [4], paving the way for the subsequent epichlorohydrin crosslinker. A crosslinker is defined as a substance that binds molecules and improves hydrogel properties. The role of crosslinker ECH is to form 3D structures in hydrogels. After forming hydrogen bonds with the cellulose, the TBPH is replaced by the crosslinker ECH. Thus, the role of TBPH is only opened up the structure of cellulose for the crosslinker.
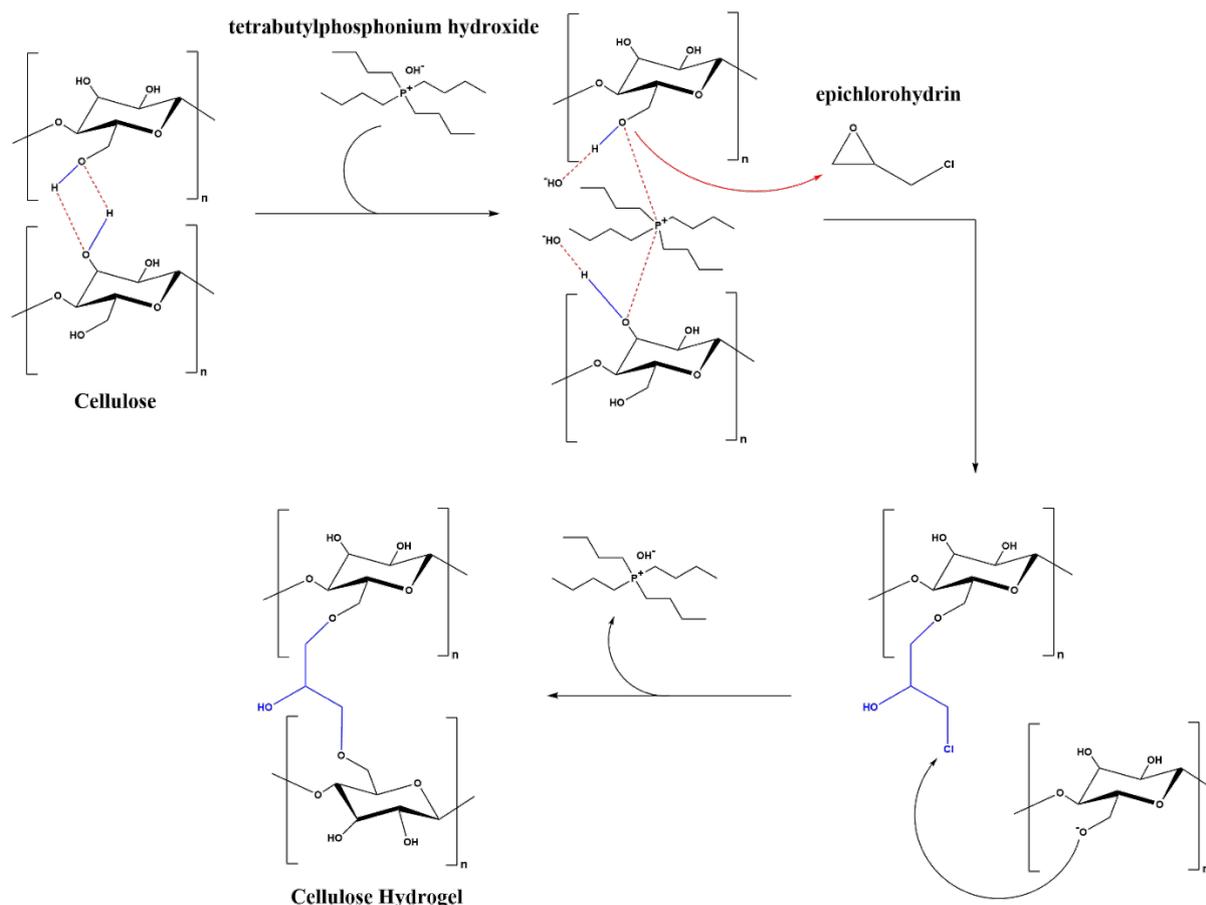
Fig. 3. Hydrogel formation mechanism
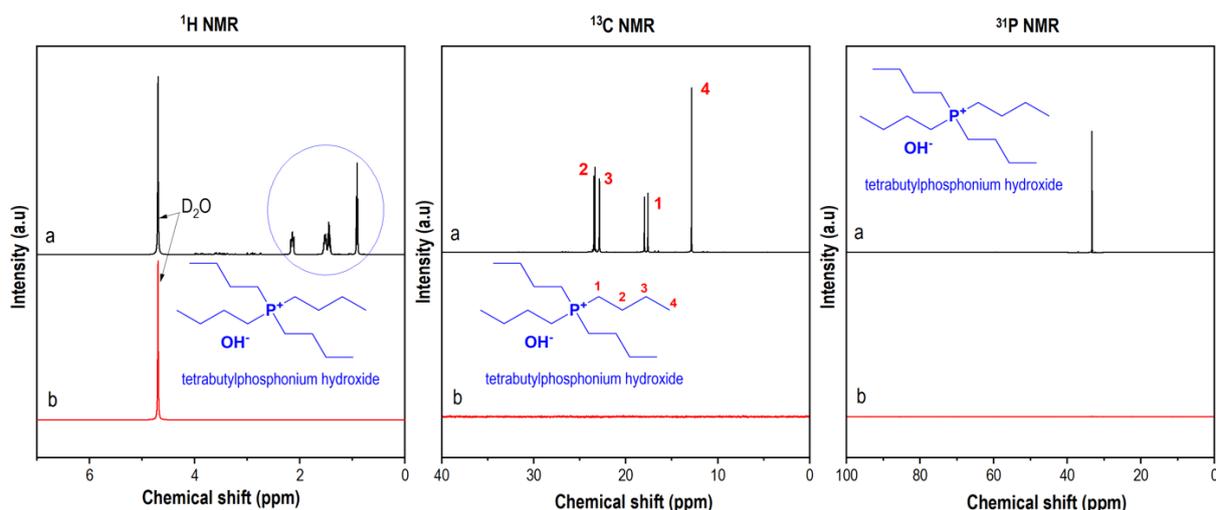
Fig. 4. NMR spectra of water containing hydrogel after washing for 1 hour (a) and 23 hours (b)

To verify the disappearance of TBPH after post-treatment process, Nuclear Magnetic Resonance ^{1}H, ^{13}C, and ^{31}P were applied (Fig. 4). The hydrogel after washing for 1 hour, which still contains the TBPH, is used as a reference for the purity hydrogel. The leftover solution is used for the NMR characterization. In the ^{1}H-NMR, the solution after 1 hour washing hydrogel still contains the signature chemical shift of the TBPH, but it is lost after 23 hours treatment. The TBPH chemical shift is identical to that of Abe's

research [4]. Furthermore, the ^{13}C-NMR showed 4 peaks, which corresponds to the three methyl groups of TBPH. In addition, ^{31}P-NMR spectrum of early washed solution also displayed signature phosphonium in TBPH structure. However, all of those chemical shift peaks disappeared over time, implying the complete removal of TBPH after the process.

Fig. 5 depicts the FTIR spectra of the extracted cellulose, the ECH crosslinker, and the hydrogel. In the spectra of ECH, we confirm that there are no OH groups in ECH structure at 3007 cm^{-1}. The band at 1432 cm^{-1} in the ECH spectrum is oriented toward the COO- symmetric stretching of the carboxyl group vibration. This carboxyl group led to hydrogen bonds for the formation of a hydrogel. The strong broadband at 3347 cm^{-1} and 3355 cm^{-1} for the cellulose and hydrogel assign to O-H hydroxyl group stretching vibration from the D-glucose units of cellulose. Hence, a band at 2898 cm^{-1} from the hydrogel spectrum is assigned to stretching vibrations of the C-H group in the glucose unit, which is also observed in the extracted cellulose spectrum at 2885 cm^{-1}. The signal of hydrogel had shifted to the lower wavenumber indicating successful crosslinking of the hydroxyl group of the cellulose. On the other hand, the signal at 997 cm^{-1} occurs to be the -C-O- group of alcohols and ethers existing in the cellulose backbone. The signal at 894 cm^{-1} is β-glucosidic linkages between the sugar units. The absorption at 1641 cm^{-1} and 1645 cm^{-1} in the

spectrum of cellulose and hydrogel can be assigned to the absorbed water. Around 2200 cm^{-1}, there were some interference in all three spectrum, which was attributed to the interference caused by diamond ATR module. In addition, the band at 1157 cm^{-1} disappears in the hydrogel indicating the crystal transformation from cellulose I to cellulose II in the hydrogels [10].

It is also worth noting that, in the hydrogel spectrum, all respective bands similar to the cellulose spectrum are slightly shifted to lower wavenumber, which can be attributed to the existence of the ECH crosslinker. However, the intensity of the bands remains the same in the hydrogel spectra.

The morphology of the extracted cellulose (Fig. 6a) and equilibrium swollen hydrogel (Fig. 6b) were investigated by SEM. SEM images of the extracted cellulose showed irregular and rough fiber cells with many attached fibril bundles, which was due to the removal of lignin and hemicellulose. After the synthesis, the hydrogel exhibited highly porous microstructure with very large pore size and evenly distributed pores in the range of approximately 100 μm in diameter.

Fig. 7 and Fig. 8 illustrate the thermograms of cellulose and hydrogel from 25 °C to 700 °C. It can be divided into two major weight loss stages, corresponding to the slow pyrolysis and fast pyrolysis stages.
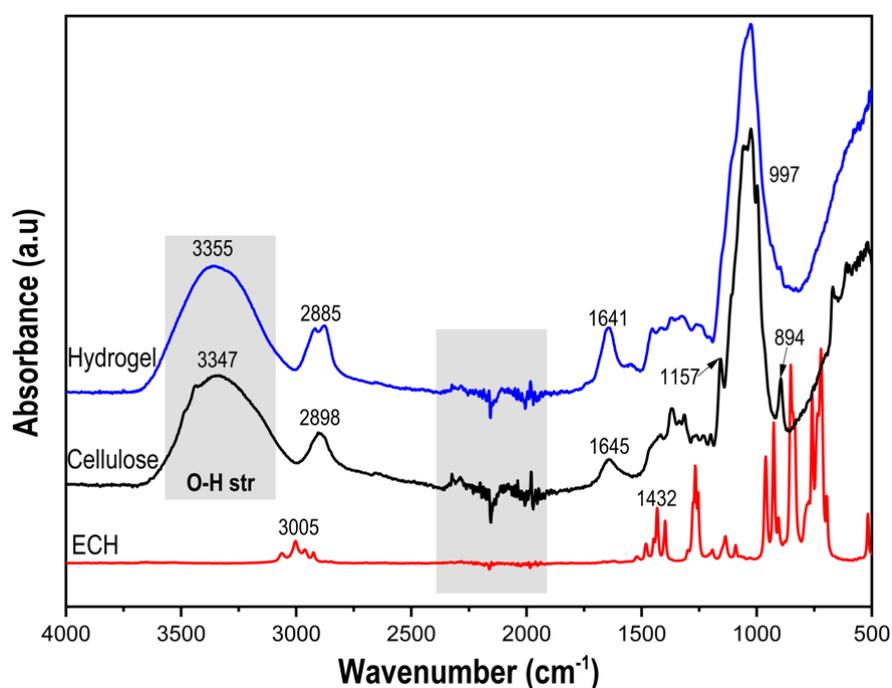
Fig. 5. FTIR spectra of cellulose, ECH crosslinker and the hydrogel
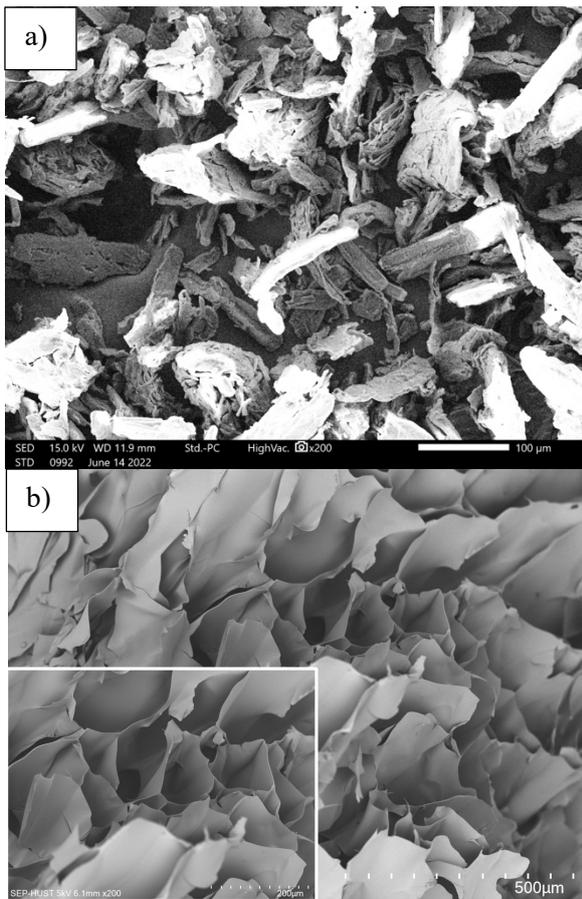
Fig. 6. SEM of (a) extracted cellulose (x200 magnification) and (b) hydrogel (x200 magnification)
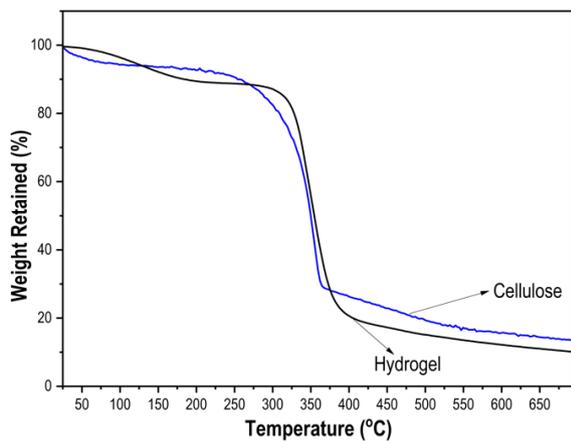
Fig. 7. TGA of cellulose and hydrogel

At the early and slow pyrolysis stage of the curve (from 25 °C to 260 °C), weight loss is mainly due to the volatilization and vaporization of moisture from the cellulosic samples. Fast pyrolysis occurred from 260 °C to 370 °C. Further weight loss was relatively fast, which was associated due to continuous decomposition of the cellulose chain.
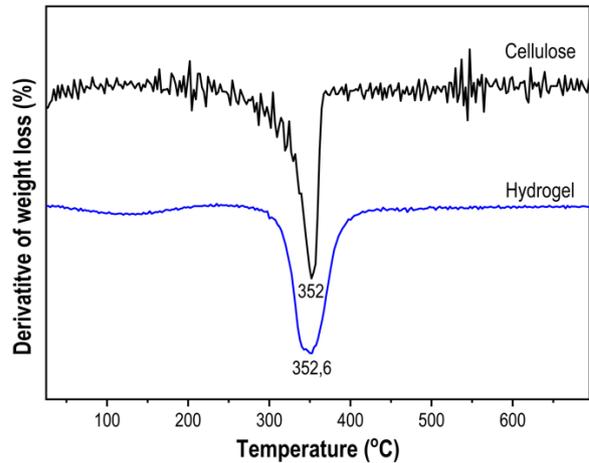
Fig. 8. DTG of cellulose and hydrogel
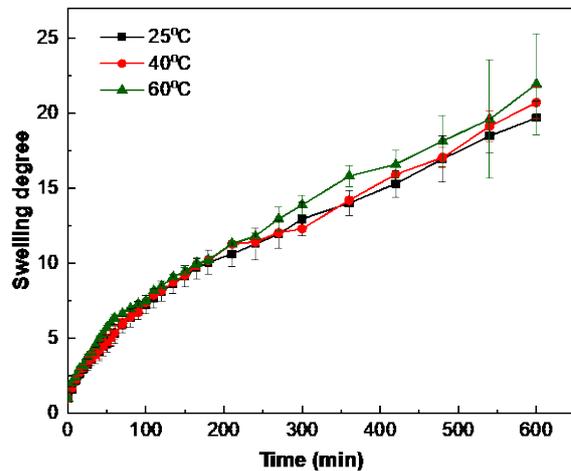
Fig. 9. The influence of temperature on the swelling properties of the hydrogel

In Fig. 8, the temperature at the maximum degradation rate did not differ significantly between extracted cellulose (352 °C) and hydrogel (352,6 °C). It is worth noting that cellulosic hydrogel has the relative close degradation temperature at 400 °C, similar to different types of hydrogels, such as physical bonding hydrogel from cellulose/Polyvinyl alcohol [5].

The swelling properties of the hydrogel was investigated in various temperature conditions to examine its effects, whereas the pH conditions were maintained at 7 throughout the process. In addition, the impact of pH to swelling properties was evaluated as well. The temperature was kept at 25 °C and the pH value was changed among acidic medium (pH = 4), neutral medium (pH = 7), and basic medium (pH = 10) (Fig. 9 and Fig. 10).
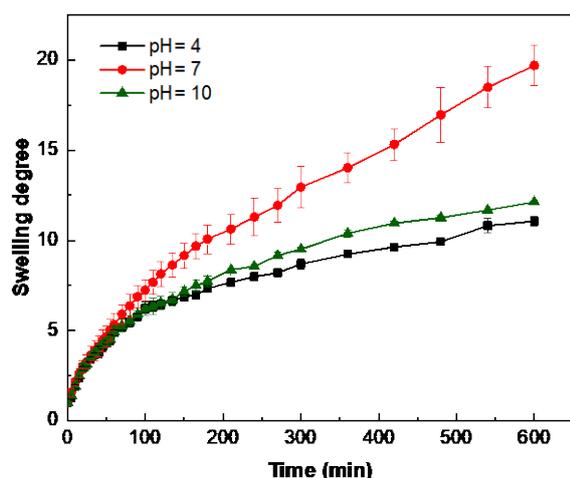
Fig. 10. The influence of pH on the swelling properties of the hydrogel

From Fig. 9, it is clear that the swelling degree slowly builds up through time at different temperatures. At lower temperature (T = 25 ºC), slow movement and diffusion of water into the hydrogel structure was caused by low internal energy and entropy. However, by rising the temperature, through the first 100 - 200 minutes, swelling degree rises fast, but it slows down as the water molecules fill in the gel network through adsorption. This increasing water uptake is owing to more space, flexible polymer chains, which is easier for water diffusion in higher temperatures. Thus, at lower temperatures, induced crosslinking by the ECH may interfere with the chain, reducing chain flexibility and water adsorption. However, at higher temperatures, secondary interactions decrease, which open up the gel matrix.

For the pH effects, temperature for the swelling process is 25 °C.

Surprisingly, huge different is noticed by different pH. In both acidic and basic condition, hydrogel shows lower swelling degree compared to an average pH = 7. It can be assumed under the neutral condition, water molecules create hydro bonds, which generate more space in the hydrogel structure. As a result, the hydrogel swells up, which not only increases the swelling degree, but also allow solvent molecules to penetrate the hydrogel [11]. As hydrogels use the backbone of ECH, it retains its electrophilic properties, which results in a lower swelling degree compared to neutral pH conditions. In base conditions, swelling degree is slightly higher than acid conditions owing to the destruction of the complex, which opens up the structure. In addition, others hydrogel using ECH as a crosslinker also shows similar behavior regarding pH-sensitive conditionds [12].

4. Conclusion

The utilization of ECH crosslinking agent for cellulose extracted from rice straw has proved to be successful, since the FT-IR spectrum of the hydrogel retains all cellulose signature bands, with only minimal shifting owing to the ECH in the hydrogel structure. The synthesized hydrogel has a high purity as demonstrated by the NMR results. The swelling degree is investigated with different temperatures and pH conditions. It is evident that under all conditions, the swelling increases moderately in the first few hours, gradually decreases after 200 minutes but still remains an upward trend. Whereas higher temperature shows better swelling degree because of the chain flexibility, the different is minimal. On the other hand, the corresponding degree of swelling under different pH conditions is remarkable. The highest swelling capacity was found at pH 7.0 and 60 ºC. These results gave handsight to the hydrogels behaviour in pharmaceutical applications, which requires different conditions.

References

[1] K. Parmar, Biomass - An overview on composition characteristics and properties, IRA - Int. J. Appl. Sci., vol. 7, no. 1, pp. 42-51, 2017.
https://doi.org/10.21013/jas.v7.n1.p4.

[2] C. L. Williams, R. M. Emerson, and J. S. Tumuluru, Biomass compositional analysis for conversion to renewable, in Biomass volume estimation and valorization for energy, IntechOpen, pp. 516, 2017.
https://doi.org/10.5772/65777.

[3] A. Brandt, J. Gräsvik, J. P. Hallett, and T. Welton, Deconstruction of lignocellulosic biomass with ionic liquids, Green Chem., vol. 15, no. 3, pp. 550-583, 2013.
https://doi.org/10.1039/c2gc36364j.

[4] M. Abe, Y. Fukaya, and H. Ohno, Fast and facile dissolution of cellulose with tetrabutylphosphonium hydroxide containing 40 wt% water, Chem. Commun., vol. 48, no. 12, pp. 1808-1810, 2012.
https://doi.org/10.1039/c2cc16203b.

[5] J. T., H.-U. Ko, X. Gao, Y. Li, S. Y. Kim, and J. Kim, Cellulose/polyvinyl alcohol-based hydrogels for reconfigurable lens, in Nanosensors, Biosensors, and Info-Tech Sensors and Systems 2016, vol. 9802, pp. 1-6, 2016.
https://doi.org/10.1117/12.2219651.

[6] S. Bhaladhare and D. Das, Cellulose: a fascinating biopolymer for hydrogel synthesis, J. Mater. Chem. B, no. 10, pp. 1923-1945, 2022.
https://doi.org/10.1039/d1tb02848k.

[7] H. Zhang, F. Zhang, and J. Wu, Physically crosslinked hydrogels from polysaccharides prepared by freeze-

thaw technique, React. Funct. Polym., vol. 73, no. 7, pp. 923-928, 2013.
https://doi.org/10.1016/j.reactfunctpolym.2012.12.014.

[8] N. D. Vu, H. T. Tran, N. D. Bui, C. D. Vu, and H. V. Nguyen, Lignin and Cellulose extraction from Vietnam's rice straw using ultrasound-assisted alkaline treatment method, Int. J. Polym. Sci., vol. 2017, pp. 1-8, 2017.
https://doi.org/10.1155/2017/1063695

[9] B. Zhang, H. Li, H. Luo, and J. Zhao, Ring-opening alternating copolymerization of epichlorohydrin and cyclic anhydrides using single- and two-component metal-free catalysts, Eur. Polym. J., vol. 134, no. 5, pp. 109820, 2020.
https://doi.org/10.1016/j.eurpolymj.2020.109820.

[10] M. A. Navarra, C. Dal Bosco, J. S. Moreno, F. M. Vitucci, A. Paolone, and S. Panero, Synthesis and characterization of cellulose-based hydrogels to be used as gel electrolytes, Membranes (Basel)., vol. 5, no. 4, pp. 810-823, 2015.
https://doi.org/10.3390/membranes5040810.

[11] R. Shah, N. Saha, and P. Saha, Influence of temperature, pH and simulated biological solutions on swelling and structural properties of biomineralized (CaCO$_3$) PVP-CMC hydrogel, Prog. Biomater., vol. 4, no. 2-4, pp. 123-136, 2015.
https://doi.org/10.1007/s40204-015-0043-1.

[12] S. Nezami, N. Nematidil, F. Farzan, F. Mirzaie, H. Sadeghi, and M. Sadeghi, pH-sensitive drug delivery systems based on CMC-ECH-CTS and CMC-ECH-CTS/Fe$_3$O$_4$ beads, Polym. Test., vol. 97, no. 3, pp. 1-13, 2021.
https://doi.org/10.1016/j.polymertesting.2021.107144.