



# Effect of Ammonium Sulfate on the Porous Creating of Regenerated Cellulose Hydrogel from Palm Oil Trunk

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## ABSTRACT

Oil palm is an oil plant which is of great importance for both the Thai and the world economies. Oil palm trees have a life span of approximately 20-25 years before a gradual erosion of yield sets in. Oil palm trunk (OPT) is an agricultural residue waste from oil palm replantation which is rich in cellulose but utilized ineffectively. One way for OPT utilization is cellulose hydrogel production. In this study, cellulose hydrogel was prepared by dissolving cellulose from OPT with 7% (w/v) of lithium chloride in dimethylacetamide (LiCl/DMAc) to create a porous hydrogel by 1, 3, 5, 8 and 10% (w/v) of  $(\text{NH}_4)_2\text{SO}_4$  for 3, 5 and 10 minutes. After that, it was found that soaking cellulose hydrogel in 8% (w/v) of  $(\text{NH}_4)_2\text{SO}_4$  solution for 5 minutes created light-browed cellulose hydrogel with an average Shore A hardness of  $41 \pm 1.13$  and a maximum swelling equal to 90%. The chemical functional group and cross-section morphology of cellulose hydrogel were determined using Attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR) and Scanning electron microscopy (SEM), respectively.

**Keywords:** Oil palm; Cellulose hydrogel; Ammonium Sulfate

## **1. Introduction**

A hydrogel is a crosslinked macromolecule used to make three-dimensional networks[1], which can absorb or swell in water or biological fluid but are not soluble in a solvent. Hydrogels are useful for applications in food, cosmetics, water treatment, sensor contact lenses, and drug delivery, because they have good biocompatibility, biodegradability, non-toxicity[2], good swelling and permeability. Common water soluble polymers are favorable for using hydrogel formations such as carboxymethylcellulose (CMC)[3], hydroxyethyl cellulose[4], and oxypropyl cellulose, methyl cellulose[5], polyvinyl alcohol (PVA), and polyethylene oxide(PEO). Moreover, biopolymer based hydrogels are an abundant renewable source from plants as well as cellulose in terms of cellulose based hydrogels.

A cellulose-based hydrogel can be prepared using a cellulose solution via a physical crosslink, because they have a lot of hydroxy groups in the molecule chain which can connect a polymer network with hydrogen bonding, both internal and external molecules. Cellulose is one of the polysaccharides which is found in plants. Moreover, cellulose is extracted from oil palm trunk(OPT) as lignocellulosic biomass material but it is not utilized effectively even though there is a large amount found in southern Thailand. OPT has high cellulose content of 42.51%[6], which is nontoxic and cheap. OPT can also be used as an alternative source of cellulose to develop hydrogel with attractive structures and properties similar to other hydrogels.

A porous hydrogel is widely utilized in different fields such as soft robotics, drug delivery, microfluidic valves, support catalysts and chromatography[7]. Several methods for creating porosity in hydrogels have been used, such as gas forming[8] and fiber bonding particle leaching[9], to fabricate homogenous macroporous hydrogels.

The particle leaching technique is the dispersion of a porogen to control the pore size of a hydrogel by immersing the polymer in the selected solution. Meanwhile, porosity is created after porogen leaching, resulting in the fabrication of a porous hydrogel. A common porogen used for this technique is a salt particle, such as inorganic porogen (KCl), because they are cheap, easy to control, have high quantity, and stability, and lead to small surface and porosity[10]. Type, amount, and molecular weight of porogens are important in influencing the porous hydrogel properties. Moreover, salt leaching has been reported to fabricate porous three-dimensional matrices in microfluidic devices[11].

This research aimed at studying the production and properties of hydrogel from the cellulose of palm plants aged over 20-25 years old with organic solvents in order to alleviate the problem of waste management in palm plantations while being able to further apply such as adsorbent and herbicide carriers. Moreover, the effects of a concentration of  $(\text{NH}_4)_2\text{SO}_4$  as salt porogen and time to creating a porous cellulose-based hydrogel were also studied.

## **2. Materials and Methods**

### **2.1 Materials**

OPT was collected from a local oil palm plantation in Chumphon province, Thailand. OPT was cut into 1 x 1 cm and was dried at 60°C. Then it was milled by a power chopping mill (DMF-20A, China). The milled OPT was sieved with a 60 screen mesh size (ASTM E11, Retsch, Germany). Then it was stored in a plastic box at room temperature.

The chemical composition of OPT such as cellulose, lignin, and extractive was determined by TAPPI T203 OM-88, TAPPI T 204 OM-98, and TAPPI T 204 OM-97, respectively. Hemicellulose was determined as described by Nantharat and coworker in 2014[12].

Sodium hydroxide (NaOH), hydrochloric (HCl), and lithium chloride (LiCl) were purchased from Loba Chemie. Sodium Chlorite (NaClO<sub>2</sub>), acetic acid (CH<sub>3</sub>COOH), and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) were purchased from Ajax Finechem, New Zealand. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was purchased from Fisher Scientific, United Kingdom. *N,N*-dimethylacetamide (DMAc) was purchased from Sigma Aldrich. Isopropyl alcohol, ethanol, and were purchased from Labscan, Ireland. Methanol was purchased from Merck. All chemicals were analytical reagent grade.

## 2.2 Cellulose extraction

The OPT was pretreated with steam-explosion at 121°C under pressure 15 bar for 15 min. and then completely dried in an oven at 105°C for 6 h. The dried sample was stored in a desiccator for further use. 10 g of dried OPT was added to 1.2% (v/v) HCl in a three-necked flask with magnetic stirring at 40-60°C for 2-3 h and reflux extraction at 100°C for 2 h. Next, 0.7% (v/v) H<sub>2</sub>O<sub>2</sub> solution was added to oil palm pulp under magnetic stirring at 80-90°C for 1.30 h under atmosphere conditions, then alkaline treatment with 3% (w/v) NaOH. The unbleached cellulose was bleached in a round bottom with 1 % (w/v) NaOCl<sub>2</sub> at a pH of 9-11 at room temperature for 2 h. The  $\alpha$ -cellulose was isolated from the bleached cellulose by dissolving in 17.5% (w/v) NaOH; subsequently, it was precipitated and filtrated. After that, the obtained  $\alpha$ -cellulose was dried in an oven at 105°C for 12 h.

## 2.3 Cellulose hydrogel preparation

0.5 g extracted cellulose was dissolved in 7%LiCl/DMAc with 10 mL at a temperature of 150°C for 1 h. It was then poured into a Petri dish in order to make cellulose hydrogel plates before getting rid of LiCl/DMAc with isopropyl alcohol, methanol, and water, respectively.

## 2.4 Creating porous hydrogel with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

Cellulose hydrogel was made porous by soaking it in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution with different concentrations of 1, 3, 5, 8, and 10% (w/v) for 3, 5, and 10 minutes. Then, the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution was removed by submerging hydrogel into 50 mL of distilled water at least 3 times. A complete removal of the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was checked with 6M NaOH.

## 2.5 Characterization

### 2.5.1 Photograph

The general external characteristics of cellulose hydrogel were recorded by taking pictures with a Canon EOS 700D camera.

### 2.5.2 Thickness

Each cellulose hydrogel was measured by an outside electronic micrometer (QLR, China). By taking three measurements, the data calculated the thickness average and standard deviation.

### 2.5.2 FTIR

The chemical function group of cellulose hydrogel was characterized with a FTIR spectrophotometer in the mode of Attenuated Total Reflectance (ATR) by placing the samples on a ZnSe mirror and then analyzing the wavenumber range of 4000-650 cm<sup>-1</sup> with 4 scans and a scan resolution equal to 16 rounds.

### 2.5.3 Gel swelling

This can be done by soaking cellulose hydrogel in 40 mL of distilled water and then weighing the wet cellulose hydrogel every hour for 12 h. Afterwards, calculate the percent of swelling of the hydrogel while comparing it with dried cellulose hydrogel using the following equation:

$$\text{Swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100$$

By determining

$W_d$  = weight of dried cellulose hydrogel

$W_s$  = weight of wet cellulose hydrogel

### 2.5.4 Hardness

The hardness of cellulose hydrogel was determined with a SHORE A durometer. Each of the samples was measured 3 times in order to find the average hardness.

### 2.5.5 Morphology

The cross-sectioned morphology of cellulose hydrogel was observed using Field emission- Scanning electron microscopy (ZEISS MERLIN Compact, German) at Walailuk University and scanning electron microscopy (JSM-5800LV, JEOL, Japan) at Prince of Songkla University. The samples were dehydrated at 70°C in an oven before attaching them to a metal stub using adhesive carbon tape. Then they were covered with gold in order to generate electricity before photographing with a scanning electron microscope (SEM)

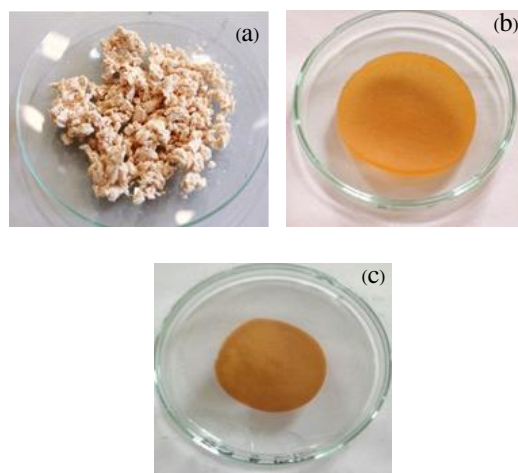
## 3. Results and Discussion

Mostly, the hydrogel can be prepared from synthesis polymers, such as polysulfone, polycarbonate, cellulose, and cellulose acetate. Oil palm plant is another interesting material that can be used as a substrate for preparing a hydrogel. Since oil palm over 20-25 years old yields low oil products, it's not economical to produce another palm tree and those aging oil palms are usually left for dead, while some are destroyed. OPT, therefore, becomes biomass material as lignocellulose composed of 36.70 ± 0.15 % of cellulose, hemicellulose at around 31.30 ± 0.18%, lignin at 15.12 ± 0.30 %, and extractive substances of 8.55 ± 0.20%, respectively.

### 3.1 Cellulose hydrogel

By preparing cellulose hydrogel from oil palms and extracting cellulose from oil palms through chemical methods, it was found that the cellulose obtained was a brown powder (Fig.1 (a)). The cellulose was then dissolved in 7% LiCl/DMAc solvent at a temperature of 150°C for 1 h before pouring into a Petri dish in order to make a cellulose hydrogel sheet (Fig.1 (b)). It

appeared that the cellulose hydrogel on the smooth sheet had a delicate brown color, a shore A hardness of 72.33 ± 0.47 and an average thickness of 0.54 ± 0.17 mm.



**Fig. 1.** (a) Cellulose from OPT (b) cellulose hydrogel and (c) cellulose hydrogel after being soaked with  $(\text{NH}_4)_2\text{SO}_4$  solution.

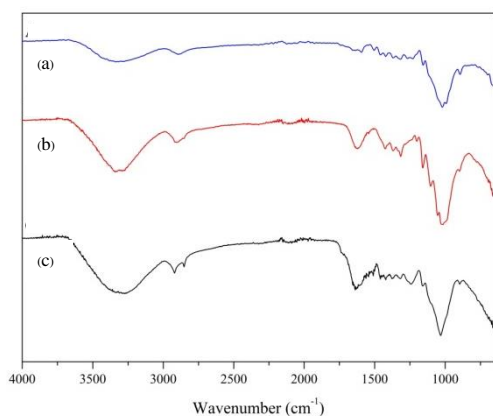
After that, the cellulose hydrogel sheet was immersed in an  $(\text{NH}_4)_2\text{SO}_4$  solution in order to create pores with different concentrations of 1, 3, 5, 8 and 10 % w/v for 3, 5 and 10 minutes (Fig.1 (c)). The results showed that cellulose hydrogel had a light brown color and its surface areas were reduced. Next, the swelling was studied; a shore A of hardness of porous hydrogel was reduced to 40% (softer) while the thickness and width expanded up to 2-3 times when compared with the original cellulose hydrogel [13].

### 3.2 Chemical structure of cellulose hydrogel

Cellulose, cellulose hydrogel and porous cellulose hydrogel with  $(\text{NH}_4)_2\text{SO}_4$  solution can prove the chemical functional group using the ATR-FTIR technique as shown in Fig.2. All samples given the identical FTIR spectrum denote that all samples were composed of similar chemical compositions. For all the spectrums shown, the broad absorption bands were found at 3,400 - 3,600  $\text{cm}^{-1}$  due to the stretching

vibration of the -OH group. The FTIR spectra, as shown in Fig.2 (b) and Fig.2 (c), in this region exhibited a change in the shape and intensity of the FTIR absorption characteristic from bleached cellulose from OPT (Fig.2(a)). This resulted from the occurrence of intermolecular interactions between the cellulose polymers within the amorphous regions.

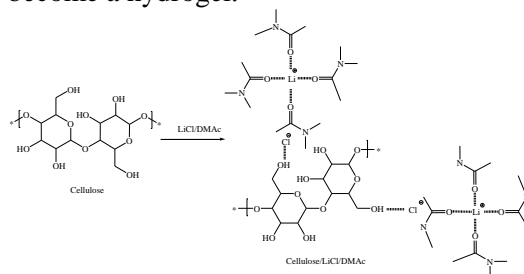
The weak absorption band at 2,800 - 2,905  $\text{cm}^{-1}$  was assigned the  $sp^3$  C-H stretching vibration of a methylene group (-CH<sub>2</sub>-) and methine group (-CH-) due to the presence of the CH and CH<sub>2</sub> groups of the anhydroglucose ring of the cellulose chain. However, the minor difference in this region of the spectra, as shown in Fig.2(b) and Fig.2(c), differs from its original cellulose (Fig.2(a)) due to the appearance of a large amount of new  $sp^3$  C-H stretching from DMAc/LiCl that caused the peak intensity to increase and split off during hydrogel formation.



**Fig. 2.** FTIR Spectrum of (a) bleached cellulose from OPT, (b) cellulose hydrogel from OPT (c) cellulose hydrogel from the of OPT that makes porous with 8% w/v of  $(\text{NH}_4)_2\text{SO}_4$  for 5 minutes.

The absorption band at 1625  $\text{cm}^{-1}$  gradually increased in the spectrum shown in Fig.2(b) and Fig.2(c). This band corresponded to the bending vibration of water molecules because of a strong interaction between the cellulose and water molecules. In addition, the absorption band

at 1,400-1,500  $\text{cm}^{-1}$  was the intermolecular hydrogen bond of the aromatic ring group at the C<sub>6</sub> [14]. The absorption band at 1,160 - 1,170  $\text{cm}^{-1}$  assigned to C-O-C stretching [15] and [16]. The band at 896  $\text{cm}^{-1}$  corresponded to C-H rocking vibration of cellulose. This shows that preparing cellulose hydrogel with LiCl/DMAc solvent is a physical transition of cellulose in which the intermolecular bond of cellulose and the bond between the chain lines of cellulose are dissolved, and the chain lines of cellulose are independent, thus being dissolved very well within this solvent [17] as shown in Fig.3. Then, it becomes a gel automatically under the merging of chain lines of cellulose, which results in self-assembly of chain lines before developing to become a hydrogel.



**Fig. 3.** Possibility solution of cellulose in LiCl/DMAc.

### 3.3 Swelling

Swelling is also one of the important parameters which influence the cellulose hydrogel porosity and the percentage of swelling as shown in Fig.4.

The unmodified cellulose hydrogel (black line) in Fig.4 shows the maximum percent of swelling was equal to 37% and capable of swelling very rapidly within 1-2 hours at the initial phase of the study because it had a strongly attached structure, thus making the polymer chain unable to move [18].

The influence of concentration and time for porous creating with  $(\text{NH}_4)_2\text{SO}_4$  solution, which is inorganic salt porogen, was also studied and is shown in Fig.4.

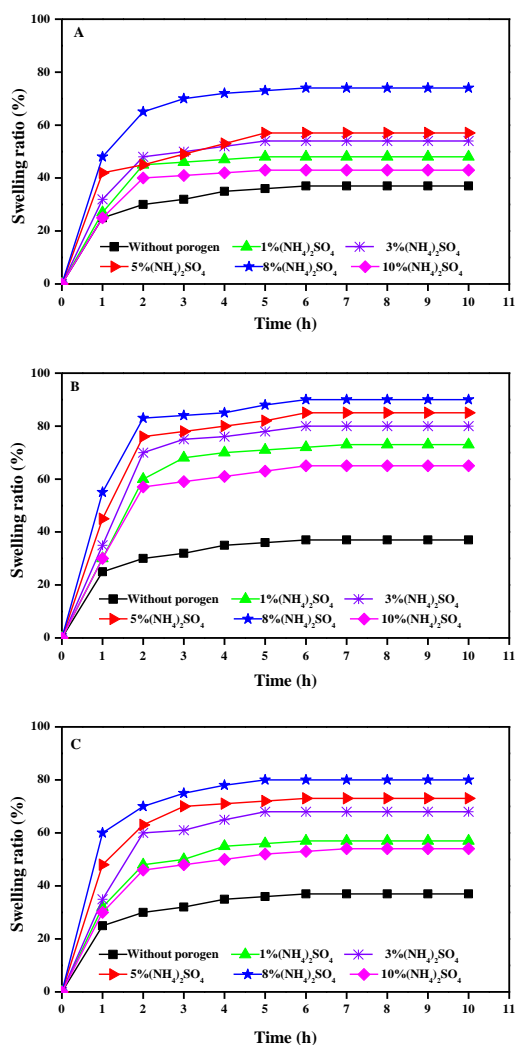
Fig. 4 (a) - Fig. 4 (c) shows the success of porous creation with the different concentrations of  $(\text{NH}_4)_2\text{SO}_4$  solution. The swelling of cellulose hydrogel was 70-90%, which was higher than that nonporous hydrogel. This indicates an influence of  $(\text{NH}_4)_2\text{SO}_4$  on the water absorption ability of the hydrogel. The  $(\text{NH}_4)_2\text{SO}_4$  may interrupt the interaction between the polymer chains, resulting in a less orderly molecular arrangement of the hydrogel polymer. Therefore, 8% of  $(\text{NH}_4)_2\text{SO}_4$  is more suited for use as a porogen to enhance a change in the morphology of a hydrogel which facilitates high swelling properties in water to the hydrogel.

Moreover, the period of time for creating a porous structure in the hydrogel at 3, 5, and 10 minutes was also studied. It was found that increasing the time for porous creating of cellulose hydrogel with  $(\text{NH}_4)_2\text{SO}_4$  solution can increase the percentage of swelling for cellulose hydrogel within only 3-5 minutes while spending 10 minutes cannot increase porous amount for cellulose hydrogel.

Thus, a period of time of 3-5 minutes is enough for preparing the cellulose hydrogel. From the result of increasing the concentration of the  $(\text{NH}_4)_2\text{SO}_4$  solution and the time for porous creating, the decrease in swelling was obtained. This could be due to a high density of crosslink internal hydrogel structure. This observation agreed with the morphology of the cellulose hydrogel from an earlier report prepared by Chang and coworkers [19].

### 3.4 Morphology of the cellulose hydrogel

Fig.5 shows the cross-sectioned morphology of the cellulose hydrogel by using the SEM with a magnifying power of 15,000x. It was found that Fig.5(a) is the morphology of cellulose extracted from OPT aged over 25 years old. These were found to have a roughed sheet.

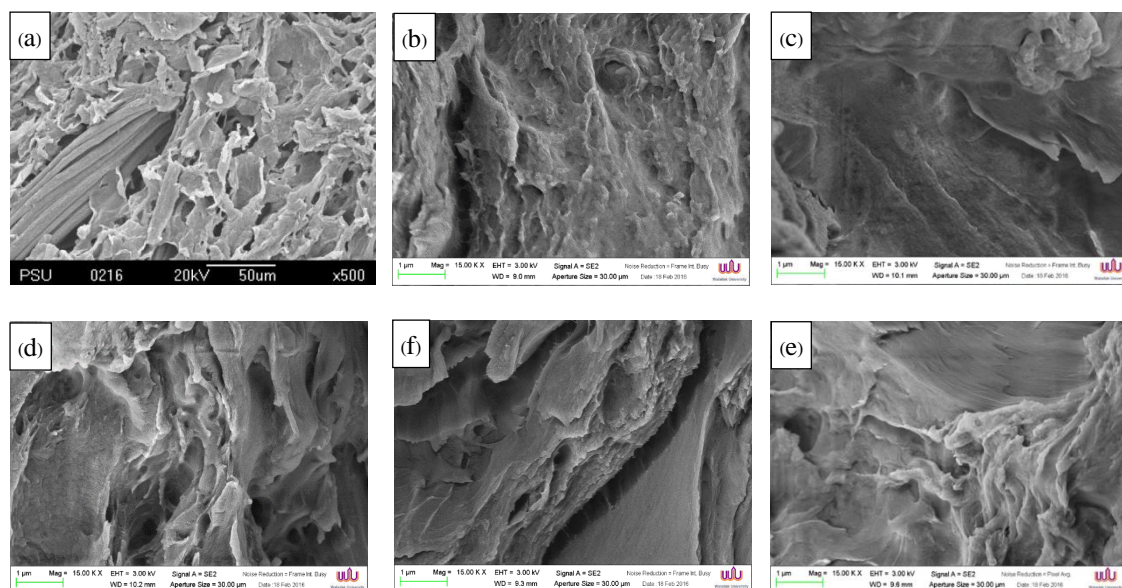


**Fig. 4.** Swelling of cellulose hydrogel with different periods of time for porous creating with  $(\text{NH}_4)_2\text{SO}_4$  solution (a) 3 minutes (b) 5 minutes and (c) 10 minutes.

Fig.5(b) - Fig.5(f) shows a cross section of cellulose hydrogel under the different conditions. Fig.4 (b) shows the physical transition of cellulose from OPT (Fig.4(a)) to cellulose hydrogel that was prepared with LiCl/DMAc solution and corresponded with the FTIR result. The cellulose hydrogel had quite a smooth surface, without appearing porous or having gaps.

However, after creating pores for cellulose hydrogel with  $(\text{NH}_4)_2\text{SO}_4$  solution with levels of concentration 1, 3, 5, 8, and 10%, it was discovered that the  $(\text{NH}_4)_2\text{SO}_4$  solution can create pores unsystematically within the structure of a cellulose hydrogel (Fig.5(c) - Fig.5(f)). The result shows that as the concentration of  $(\text{NH}_4)_2\text{SO}_4$  solution increases, making pores within the structure of hydrogel increases alike. And, the concentration that made the hydrogel most porous was the 8%  $(\text{NH}_4)_2\text{SO}_4$  solution,

diameter and was distributed throughout the areas. With the 10%  $(\text{NH}_4)_2\text{SO}_4$  solution, the porosity of cellulose hydrogel also decreased as the cause of the swelling ratio decreased. Moreover, it was found that increasing the time for soaking from 5 to 10 min could not support a porous creation because of the emergence of conglomerating cellulose and the lack of balance between the rate of pores and quick contraction [20].



**Fig. 5.** Cross section morphology of (a) Cellulose from OPT (b) cellulose hydrogel (c) 1% w/v  $(\text{NH}_4)_2\text{SO}_4$  for 5 minutes (d) 8% w/v  $(\text{NH}_4)_2\text{SO}_4$  for 5 minutes (e) 8% w/v  $(\text{NH}_4)_2\text{SO}_4$  for 10 minutes (f) 10% w/v  $(\text{NH}_4)_2\text{SO}_4$  for 5 minutes.

#### 4. Conclusions

According to this study, cellulose hydrogel of OPT was prepared by extracting cellulose from oil palm with chemical methods while preparing hydrogel from cellulose with a mixed solvent of 7 % (w/v) LiCl/DMAc at a temperature of 150°C for 1 h. Then, it was found that cellulose hydrogel had a swelling ratio capacity of only 37%. So, the porous hydrogel was increased to cellulose hydrogel with an 8% of  $(\text{NH}_4)_2\text{SO}_4$  solution for 5 minutes. And then, this showed

the maximum percent of swelling at 90%, thus showing that  $(\text{NH}_4)_2\text{SO}_4$  functions as an obstructing binding force between polymer chains, thus resulting in a reduction of orderliness for arranging the polymer chain, which is subsequently responsible for inducing water absorption more than ever. Moreover, creating pores for over 5 minutes would lead to the conglomeration of cellulose while lacking the balance between the rates of manifesting pores together with the rapid contraction of the hydrogel.

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