Preparation and properties of regenerated cellulose hydrogels

L Zhou¹, F Xie¹, H Li¹, W Li¹, W J Li¹,², * Y W Li³

¹Key Laboratory of Display Materials & Photoelectric Devices, School of Materials Science and Engineering, School of Chemical and Tianjin University of Technology, Tianjin 300384, PR China.
²Zhejiang-California International nanosystems Institute, Zhejiang University, Hangzhou, 310012, PR China.
³Shandong Yingli Industrial CO.LTD, Shandong 262700, PR China.

E-mail: liwj@tjut.edu.cn

ABSTRACT. The regenerated cellulose (RCE) hydrogels were successfully prepared via an easy and green environmental method in N-methylmorpholine-N-oxide (NMMO) aqueous solution. The effect of cellulose content on the thermostability properties, swelling behavior and retention rate of hydrogels was investigated. The thermostability of RCE hydrogels was slightly enhanced with the addition of 8 wt% cellulose, the highest decomposition temperature rose from 335 °C to 352 °C, and the least heat loss is about 75.60%. The equilibrium swelling ratio increases from 394.12% for 3% cellulose hydrogels to 619.46% for 8% cellulose hydrogels. The retention ratio increases from 1.13% to 28.46%.

1. Introduction
In the past decade, the hydrogels as new biomaterials prepared from natural polysaccharide have been extensively studied. It has a three-dimensional cross-linked network, only swelling but not soluble in solvents. Hydrogels have attracted wide applications in water treatment, food, cosmetics, sensors, contact lenses, tissue engineering and drug delivery systems due to their excellent hydrophilic properties, biocompatibilities, permeability and high swelling ratio [1,2]. As the ideal green environmental material, the cotton pulp with the high cellulose content is nontoxic and cheap. Macromolecular cellulose composed of glucose molecules and hydrophilic hydroxyl groups is a kind of regularity of the three-dimensional linear polymer, in which the main anhydrous glucose residues through β (1-4) glycosidic bond connect with D - pyran glucose [3,4]. Thus, the cellulose hydrogel and a polymer network system can be formed by the hydrophilic carboxyl groups combined with water molecules. Normally, the soft and white cellulose hydrogel can absorb a lot of water and maintain a certain shape. The mechanism of the hydrogel is the state of the swelling cellulose molecular chain with hydroxyl hydrogen bonding interaction connecting, gathering, and twining to form a hydrogel [5]. N-Methylmorpholine-N-oxide monohydrate (NMMO) is an effective “green” solvent for cellulose in industrial fiber-making. The NMMO shows low toxicity, high thermal stability, and the possibility of being recovered and reused. It affects hydrogen bonds and weakens van der Waals forces between the cellulose chain molecules, thus changing the cellulose structure [6].
2. Materials and methods

2.1. Preparation of RCE hydrogels
About 1g of CE was mixed with 0.02g of ascorbic acid. Then about 33.30g of an aqueous solution of NMMO (33.3g, 25g, 19g, 15.7g, 11.48g, respectively) was added to the mixture in a beaker. After that, the beaker was placed in a vacuum oven set at a temperature of 110oC and the vacuum of -0.1MPa. The heating was carried out until the mixture was transformed into a uniform transparent amber solution.

Finally, the deionized water was introduced into the beaker, and the deionized water was changed every 8h for the formation of the opalescent hydrogel containing about 3% of RCE.

The procedure was repeated by using various amounts of an aqueous solution of NMMO (25.00g, 19.00g, 15.70g, and 11.48g) to produce hydrogel containing about 4, 5, 6, and 8% of RCE, respectively.

2.2. Swelling ratio
The dried hydrogels were immersed in distilled water at room temperature. The weight of the ternary hydrogels was repeatedly measured every hour after the excess water on the surfaces was wiped with filter paper. Swelling ratios (SR) was calculated as follows:

\[
SR(\%) = \frac{W_t - W_0}{W_0} \times 100\%.
\]

where the \(W_t\) is the weight of the swollen hydrogel at a designated time \(t\) during swelling and the \(W_0\) is the weight of the dried hydrogel.

2.3. Retention test
The Albumin Bovine V (BSA) powder (0.15g) was dissolved in the buffer solution (PH=7.4) for preparing the basic protein buffer (1.5 g/l). The buffer solution was composed by monosodium orthophosphate and disodium hydrogen phosphate. The concentration of BSA before and after filtration was determined by recording the protein buffer solution absorption wavelengths at 280nm, using the ultraviolet-visible spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co. Ltd). The retention rate (R) was calculated as follows:

\[
R(\%) = \frac{C - C_0}{C} \times 100\%.
\]

where the \(C\) and \(C_0\) are the concentration of initial and filtered protein buffer solution.

3. Results and Discussion
The SEM image of the regenerated cellulose (RCE) hydrogels is shown in Fig. 1. It can be seen that the cellulose fibers with one-dimension are interfingering with each other and forming a three-dimensional network. Many porous structures with varying sizes in the hydrogels can be observed. After the water evaporates, lots of holes can be preserved in dried hydrogels due to the freeze-dried method, which keeps the hydrogels dry in the original state. Therefore, the numerous water molecules could easily diffuse into hydrogels to form the large pores, leading to the higher swelling ratio.

The FTIR spectrum of the regenerated cellulose (RCE) hydrogel is shown in Fig. 2. The broad absorption bands of the hydrogels at 3000–3500 cm\(^{-1}\) are assigned to stretching of a large number of hydroxyl groups on the cellulose. The stretching vibration of CH 2 is evidenced by the appearance of the absorption peaks at 2920 cm\(^{-1}\). The band observed at 1625 cm\(^{-1}\) and 1375 cm\(^{-1}\) in the cellulose hydrogels can be attributed to COO\(^{-}\) stretching and bending, respectively. The results indicate that the carboxyl groups and hydroxyl groups existed in the hydrogels.
Fig. 3 shows the regenerated cellulose (RCE) hydrogels' TG curves and DTG curves, respectively. From the figure, we can see that the thermostability of RCE hydrogels are getting better with the cellulose content increasing. The least thermal degradation is 65% with 8% RCE hydrogels. The highest decomposition temperature is rising from 342°C to 352°C. The increase in the thermal stability may be due to the increase of cellulose content in the hydrogel. As the cellulose content is increased, the number of OH groups also increase. Since the OH groups are responsible for the formation of hydrogen bonding between the cellulose molecules, increase the amount of OH groups increases the
number of hydrogen bonds between the molecules and enhanced the intermolecular force so that the thermostability of RCE hydrogels is improved.

![Graph showing weight vs. temperature](image)

**Figure 3.** The regenerated cellulose (RCE) hydrogels’ TG curves (1) and DTG curves (2): 4% RCE (a); 5% RCE (b); 6% RCE (c); 8% RCE (d).
Fig. 4 shows the typical swelling curves of the hydrogels with various contents of cellulose in distilled water. It is evident that the water uptake rate and equilibrium swelling ratio of hydrogels gradually increase with the increase of cellulose. This phenomenon is ascribed to the increase in the number of hydrophilic hydroxyl groups and the three-dimensional cross-linked network structure of hydrogels. For cellulose hydrogels, the rapid initial absorption occurs in the first 10 h and then gradually increases to reach equilibrium. The absorption rate is slightly increased with the increasing cellulose contents due to the fact that the water molecules are easily inhaled in the loose hydrogel at the commencement of absorption. When the absorbed water reached a certain extent, the original molecular chains are gradually stretched. The pressure is increased as the inhaled water increase, which prevents the additional water from being absorbed and penetrated through into matrix. Moreover, the equilibrium swelling ratio increases from 394.12% for 3% cellulose hydrogels to 619.46% for 8% cellulose hydrogels. The retention test of 3%, 4%, 5%, 6% cellulose hydrogels are 1.13%, 6.17%, 16.79% and 28.46%, respectively. It is obvious that the retention rate of hydrogels gradually increases with the increase of cellulose.

4. Conclusions
In summary, regenerated cellulose (RCE) hydrogels were successfully prepared via a straightforward and green environmental method in N-methylmorpholine-N-oxide (NMMO) aqueous solution. The thermostability, the equilibrium swelling and the retention ratios of RCE hydrogels increased with the cellulose content.

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