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Short communication

Cellulose hydrogels prepared from micron-sized bamboo cellulose fibers

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ABSTRACT

We demonstrated for the first time that dimensionally stable hydrogels could be obtained from bamboo pulp fibers through dialysis against distilled water followed by a short time of ultrasonic treatment. Micron-sized short fibers rather than cellulose nanofibrils constituted the majority of fibers in the hydrogels. During the pulping process with HNO_3 and $KClO_3$, carboxylic groups could be introduced to cellulose due to the mild oxidation of hydroxyl groups. When presented in aqueous NaOH, the carboxylic groups could be converted into their sodium salt form. The subsequent dialysis treatment against water made the negatively charged —COO^- groups extensively exposed. The negatively charged cellulose fibers could induce considerable electrostatic repulsion between them, which was discovered to govern the formation of hydrogels. In addition, it was revealed that homogeneous hydrogels could be formed when the pH was at 7, 9 and 11. However, when salt was added, no dimensionally stable hydrogel was obtained.

1. Introduction

Hydrogels are defined as a three-dimensional polymer network containing a large amount of trapped water (Chang & Zhang, 2011). As new biological materials, cellulose-based hydrogels have been developed rapidly in the last decade. Cellulose hydrogels are generally produced from cellulose solutions (Zhou, Chang, Zhang, & Zhang, 2007). Recently, nano-sized cellulose was revealed to have the ability to form hydrogels under certain conditions. For example, Abe and Yano (2011) reported that a 0.8 wt% cellulose nanofibrils (CNFs) suspension, which exhibited a high viscosity but still possessed fluidity, could become hydrogels when treated with 9–15 wt% alkaline as a result of the aggregation and axial shrinkage of nanofibrils. Chen, Yu, and Liu (2011a) discovered that CNFs aqueous suspension with an average fiber width of 2–4 nm would lose flowability and turn into a viscous hydrogel when CNFs content was above 1.0 wt%.

As an alternative approach, we hereby reported bamboo cellulose fibers, which were produced from the pulping process with $HNO_3/KClO_3$, could form stable hydrogels through dialysis against water followed by a short time of ultrasonication. The possible gelation mechanism for this novel hydrogel was discussed. In addition, the influence of pH and salt on the formation of cellulose hydrogel was investigated. Compared with most methods for preparing cellulose hydrogels, which required complex and difficult dissolution processes usually with harmful solvents, the physical approach proposed here was quite environmentally friendly and effective. Also, in contrast to the emerging CNFs-based hydrogels, our hydrogels were mainly composed of cellulose fibers with diameters in the micron size. Because the isolation of CNFs was high energy consuming, the present approach seemed to be very energy-efficient.

2. Experimental

Cellulose fibers were extracted from bamboo powders using the $HNO_3/KClO_3$ method (Liu, Zhong, Chang, Li, & Wu, 2010). The removal of lignin and hemicellulose was confirmed by FT-IR and XRD analysis (Figs. S1 and S2). A 0.85 wt% cellulose fiber suspension was mixed with NaOH (1.2 wt% in the suspension) and then dialyzed against deionized water for 48 h to reach a pH value around 7. To prepare cellulose hydrogel, the cellulose suspension was subjected to ultrasonication at 1200 W for 8 min. Gelation was evidenced when the ultrasonicated cellulose suspension was kept still for 5 min.

3. Results and discussion

The obtained dimensionally stable cellulose hydrogel, which was cut off from a cylinder shape hydrogel, was presented in Fig. 1d.

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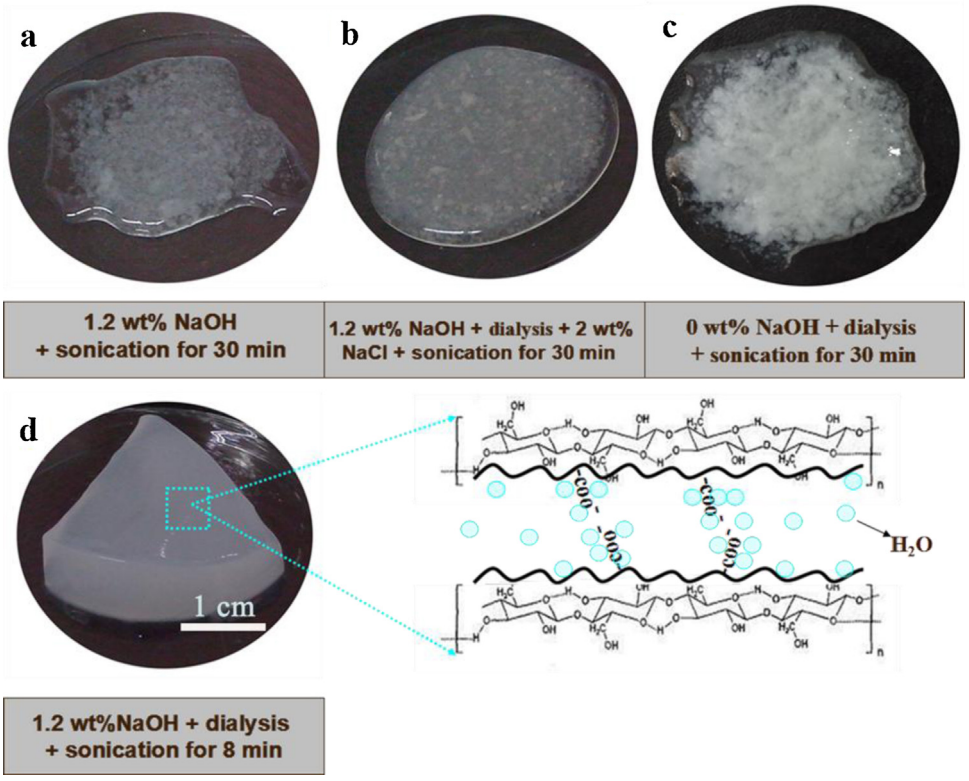

Fig. 1. Modulating the macroscopic gelation properties of cellulose hydrogels at different conditions ((a)–(d)) and a scheme for the possible gelation mechanism (d).

This hydrogel exhibited high water affinity with a swelling ratio of 230. It only shrank slightly with approximately one-third volume shrinkage after 6 months in ambient conditions. In the contrast, no gelation was observed for cellulose samples either without dialysis treatment or without the addition of NaOH prior to dialysis or with the addition of NaCl after dialysis even if a much longer time (30 min) of ultrasonication was applied (see Fig. 1a–c).

As reported, single bamboo cellulose fibers after $HNO_3/KClO_3$ extraction have lengths in the range of 0.01–1 mm, which were shorter than those of multicellular plant fibers such as flax, and the widths were about 10–50 μm (Liu, Song, Anderson, Chang, & Hua, 2012). Compared with other methods such as NaClO and H_2O_2/HAc (acetic acid), the $HNO_3/KClO_3$ method could isolate bamboo cellulose fibers with lower surface roughness (Cheng, Wang, & Cheng, 2012). The morphologies of purified cellulose fibers and cellulose hydrogel were visualized by optical microscope. Fig. 2a shows that bamboo cellulose fibers were comprised of two different types of cells, fibrous cells and rectangular cells, which were regarded mostly as fibers and parenchyma cells, respectively (Chen, Yu, Li, Liu, & Li, 2011b). The rectangular cells almost disappeared and the long cellulose fibers were shortened after ultrasonication (Fig. 2b). Such morphological changes were further verified by SEM. Fig. 2c shows more details of the two different bamboo cells. After ultrasonication, many short fibers were produced (Fig. 2d). The inserted zoom in SEM image indicated there were also a few CNFs generated during processing. Although it had been recognized that CNFs had the ability to form hydrogels, the concentration of CNFs usually had to be higher than 1 wt% to establish an effective network structure through entanglements and hydrogen bonding (Chen et al., 2011b). However, the CNFs concentration in our hydrogels was much less than this critical point, since the overall cellulose concentration was 0.85 wt% here. A possible underlying mechanism for this gelation phenomenon was assumed (Fig. 1d). During the cellulose extraction process, a limited number of carboxylic groups were generated due to the presence of oxidizing agents ($KClO_3$ and HNO_3). The absorption band at 1610 cm^{-1}, which could be assigned to the C=O stretching of carboxylate ions (Bulota, Tanpichai, Hughes, & Eichhorn, 2012), became much stronger in the FT-IR spectra of extracted cellulose and cellulose hydrogel (Fig. S1). It suggested that the cellulose fibers were oxidized to some degree during the pulping process (Fujisawa, Okita, Fukuzumi, Saito, & Isogai, 2011; Barbucci, Magnani, & Consumi, 2000). Moreover, ζ-potential measurements (Fig. S6) confirmed the purified fibers were negatively charged (−6.95 mV). When NaOH was added in the fibers suspension, the —COOH could be ionized to $—COO^-Na^+$. The movable Na^+ ions could be partially removed during dialysis. After dialysis, the ζ-potential of cellulose increased to −8.13 mV (Fig. S6). However, compared with TEMPO-oxidized cellulose whose ζ-potential could be as high as −75 mV (Okita, Saito, & Isogai, 2010), the $HNO_3/KClO_3$ extracted bamboo cellulose exhibited a much lower ζ-potential. Previously, Crawford, Edler, Lindhoud, Scott, and Unali (2012) had reported the gelation of TEMPO-oxidized CNFs with the addition of anionic surfanctant micelles. They found the gelation was more likely to follow the depletion flocculation mechanism (Sun & Raghavan, 2010). The repulsion between micelles of anionic surfactant and oxidized cellulose nanoparticles would result in segregation of both species into smaller volumes of solution, raising the apparent volume fraction and leading to gelation. In similar manner, the electrostatic repulsion induced by the negative charges on the surface of cellulose fibers, further strengthened via dialysis, could weaken the agglomerate tendency among cellulose fibers and enhance the segregation. The network became more opened, leading to a higher water uptake. Besides, the presence of $—COO^-$ also made its water affinity to be extensively improved (Barbucci et al., 2000). In addition, the cutting of cellulose fibers and the generation of tiny fibrils during ultrasonication would remarkably increase the fibers' specific surface area. It was conducive for the negative charges to be exposed and trapping more water. Consequently, the cellulose fibers, with enhanced electrostatic repulsion and water uptake, were possible to form hydrogels even if their carboxyl

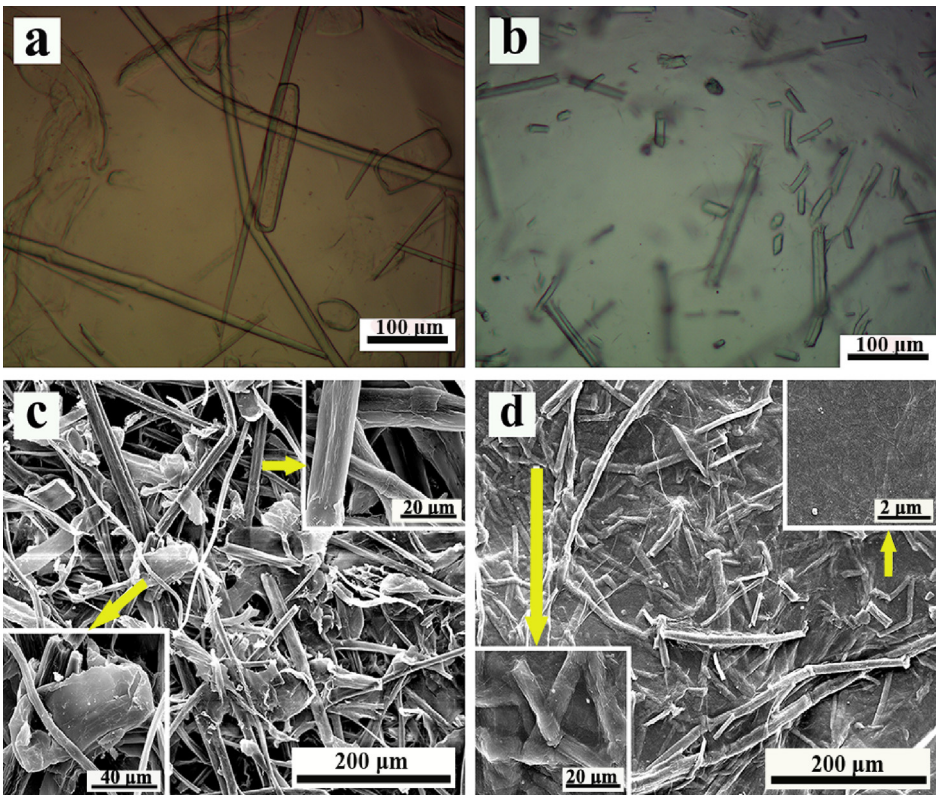

Fig. 2. Optical microscope images for (a) the purified cellulose fibers and (b) the obtained hydrogel; SEM images of (c) purified cellulose fibers and (d) freeze-dried hydrogel.

content (2.85%) was much lower than that (22%) of TEMPO-oxidized cellulose (Crawford et al., 2012).

The mechanical properties of hydrogels can be reflected by dynamic oscillatory rheology (Anderson, Andukuri, Lim, & Jun, 2009). In general, a certain gel stability can be assumed if $G' \geq 10$ Pa (Anderson et al., 2009). The G' of our cellulose hydrogel (gel-02) was about 35 Pa, exhibiting relatively stable gelation behavior. It was also discovered that the longer the ultrasonication time, the more stable the hydrogels. For classical viscous fluids, the elastic storage (G') and loss modulus (G'') are frequency-dependent, that is, $G' \propto \omega^2$ or $G'' \propto \omega^2$ as a function of frequency and $G' \ll G''$. But an ideal gel behaves elastically and $G' \propto \omega^0$, that is, storage modulus is frequency-independent (Klemm et al., 2011). Fig. 3 shows that the G'' plots were always lower than G' plots throughout the applied frequency for all hydrogels, indicating an elastic behavior with a comparatively small dissipation in energy. The G' was almost frequency-independent. These results revealed that a stable network was formed (Huang, Chen, Lin, Hsu, & Chen, 2010). The increase of G' for hydrogels prepared with a longer ultrasonication time indicated the hydrogels became more stable. Cox–Merz empirical rule could be used to correlate the steady-flow viscosity with the dynamic viscosity (Cox & Merz, 1958). For gel structures, the complex dynamic viscosity was a monotonically decreasing function of applied frequency. Fig. 3b depicts the Cox–Merz plots

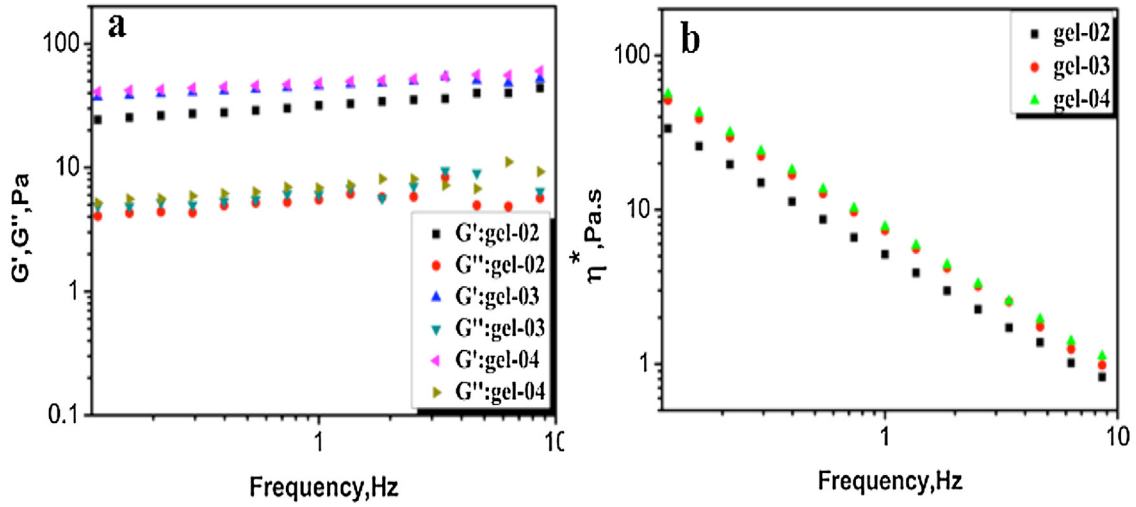

Fig. 3. (a) The elastic storage modulus (G') and loss modulus (G'') of cellulose hydrogel formed after ultrasonication for 8 min (gel-02), 15 min (gel-03) and 30 min (gel-04) as a function of frequency. (b) Complex viscosity of gel-02, gel-03 and gel-04 as a function of frequency.

of the studied materials. All hydrogels showed shear thinning properties. Also, the complex viscosity increased when a longer ultrasonication time was applied.

The influence of pH and salt concentration on the hydrogel formation was examined. Homogeneous hydrogels with stable dimensions could be formed when the pH was at 7, 9 and 11 (Fig. S3). However, both elastic storage modulus and complex viscosity of the hydrogel decreased with the increase of pH, indicating a less stable hydrogel structure at higher pH (Fig. S4). On the contrary, when pH was at 3, 5 and 14, only isolated aggregates like microgels were obtained (Fig. S3). This was because in the low pH region —COOH rather than —COO^- were presented in cellulose, leading to reduced electrostatic repulsion and water affinity. When pH was high (pH = 14) or by adding 0.1–0.9 wt% NaCl (Fig. S5), no dimensionally stable hydrogels could be formed as well. In colloidal systems, the effect of increasing ionic strength is expected to cause collapse of the double layer on charged particles allowing contact between fibers (Crawford et al., 2012). Thus, the formation of aggregates upon addition of salt is not surprising.

4. Conclusion

In summary, we have demonstrated an alternative approach to fabricate hydrogels from bamboo pulp fiber suspension through dialysis followed by a short time of ultrasonication. Bamboo cellulose fibers were mildly oxidized during the pulping process with HNO_3 and $KClO_3$, introducing —COOH groups on fiber surface. The subsequent alkali treatment changed the —COOH groups into their sodium salt form. After dialysis, negatively charged —COO^- groups could be exposed. Further ultrasonic treatment resulted in dimensionally stable hydrogels. The rheological measurements revealed a true gel structure of the hydrogel. Moreover, it was found that homogeneous hydrogels could be formed when the pH was at 7, 9 and 11. However, no dimensionally stable hydrogels were formed when salt was added. The electrostatic repulsion between negative charges on the cellulose fibers was believed to govern the formation of hydrogel.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.08.012.

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