



Fabrication of cellulose self-assemblies and high-strength ordered cellulose films



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ABSTRACT

Based on the formation of cellulose hydrogels in NaOH/urea aqueous solvent media, cellulose self-assembly precursor is acquired. It is proved that the water uptake capability of the cellulose hydrogels depends highly on the cross-link degree (CLD) of cellulose. With varying CLD and concentration of cellulose, a variety of morphologies of cellulose self-assemblies, including sheets with perfect morphology, high-aspect-ratio fibers, and disorganized segments and network, are formed through evaporation. Furthermore, cellulose films are fabricated by diecasting and evaporating the cellulose hydrogels, resulting in a 3D-ordered structure of closely stacking of cellulose sheets. The mechanical test indicates both tensile strength and flexibility of the cellulose films are greatly improved, which is attributed to the formation of the orderly stacking of cellulose sheets. The study is expected to lay an important foundation on the preparation of ordered and high-strength cellulose materials.

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1. Introduction

As the main constituent of wood and plants, cellulose is an almost inexhaustible polymeric raw material on the earth. It has a fascinating structure and is highly biocompatible and easily biodegradable. It was reported that the elastic modulus of the crystalline region of cellulose might reach the level as high as 100–200 GPa, and the density as low as 1.6 g cm^{-3} (Šturcová, Davies, & Eichhorn, 2005; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Eichhorn, 2012). These excellent properties make cellulose a focus of current researches in material preparation (Chang, Duan, & Zhang, 2009; Morandi, Heath, & Thielemans, 2009; Saito, Uematsu, Kimura, Enomae, & Isogai, 2011; Chen, Yu, Li, Liu, & Li, 2011; Fox et al., 2012). Especially, due to possessing large amounts of hydroxyl groups, cellulose is a good object for chemical modification, which endows it a wider range of applications, such as being used as reinforcement, thickener, emulsifier, and stabilizer,

etc (Habibi, Chanzy, & Vignon, 2006; Sun, Sun, Wei, Liu, & Zhang, 2007; Shahin, Nicolai, Benyahia, Tassin, & Chassenieux, 2013). Up to date, cellulose is becoming one of the most promising candidates to replace petroleum-based materials in both daily life and industry production.

However, comparatively strong H-bonds between cellulose chains would be formed because of the abundant hydroxyl groups on cellulose. Therefore, a quite firm network can be established in cellulose, leading to poor solubility of cellulose in both aqueous media and most of common organic solvents. This inhibits its further application. Moreover, although cellulose has been investigated to a large extent, due to the complexity of H-bonds, its fine structural features have not been identified with absolute clarity (Kroon-Batenburg & Kroon, 1997; Langan, Nishiyama, & Chanzy, 1999; Nishiyama, Langan, & Chanzy, 2002).

Therefore, one of attractive issues on cellulose is to search for its solvent systems. As for that, a few solvents have been developed, such as *N,N*-dimethylacetamide (DMAc)/LiCl system, *N*-methylmorpholine *N*-oxide (NMMO)/water system, and ionic liquids, etc (Roder, Morgenstern, Schelosky, & Glatter, 2001; Swatloski, Spear, Holbrey, & Rogers, 2002; Kulpinski, 2005; Zhu et al., 2006). The dissolution of cellulose in these systems is attributed to the coordination effect between hydroxyl groups and some certain small ions (e.g., chloride ions, sodium ions, and so

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on). As one of 'green' solvents, the NaOH/urea/water system has been paid much attention to recently because of the comparatively simple and rapid dissolving process (Cai & Zhang, 2006; Cai et al., 2008). In the solvent, urea, which plays a role of inclusion around cellulose molecules, inhibits the aggregation of cellulose (Cai & Zhang, 2005). This is known as a pioneering work on further utilization of cellulose (Liu et al., 2008; Li et al., 2010; Shi et al., 2011; Cai et al., 2012; He, Xu, & Zhang, 2013; He et al., 2014). However, in all of these solvent systems, serious problems may still exist in the preparation of cellulose materials due to the strong H-bond interaction. Generally, random flocculi without any strength could be formed when a cellulose solution is diluted by water, due to the sharp change of the micro-environment around cellulose molecules. Besides, unordered hydrogels would come into being when a cellulose solution is dipped into a certain coagulating bath, resulting in final unordered dried cellulose materials (Zhang, Mao, Zhou, & Cai, 2005; Geng et al., 2014).

However, in fact, cellulose has the potential to construct ordered structure via self-assembly. For example, naturally occurring cellulose possesses a semi-crystalline structure where highly ordered regions (crystallites) distribute within unordered domains (amorphous phase). Both crystalline and amorphous regions together construct an ordered rodlike (or fibrous) structure with high aspect ratio. This is the common morphology of cellulose in nature (such as in plant cell, bacteria and some sea animals (tunicates)), which plays an important role in protecting and supporting living cells. Another typical example is the self-assembly of cellulose nanocrystals (CNCs). When reaching a certain concentration in aqueous media, CNCs are able to self-assemble into cholesteric liquid crystalline phase (Shopsowitz, Qi, Hamad, & MacLachlan, 2010; Shopsowitz, Hamad, & MacLachlan, 2012; Giese et al., 2013). In the latest researches, it has also been shown that a 2D sheet-like skeleton structure can be produced by carefully controlling the content of CNCs (Heath & Thielemans, 2010; Chen et al., 2011; Han, Zhou, Wu, Liu, & Wu, 2013). Yet for regenerated cellulose originating from dissolved cellulose, an unordered 3D network rather than ordered or organized cellulose structures would form because of the fast physical aggregation of cellulose molecules during regenerating process due to the strong H-bond interaction.

In our opinion, a possible approach to obtain or control ordered structures of regenerated cellulose is to restrain the rapid physical aggregation caused by strong H-bond interaction within dissolved cellulose. In this work, NaOH/urea aqueous media is selected as the solvent of cellulose because of its unique merits. In order to inhibit cellulose from quick flocculation when changing pH, or from unordered gelation in coagulation baths, cellulose molecules would be chemically cross-linked in the solvent media before the subsequent self-assembling. Then a 'top-down' method (ultrasonication) is adopted to shred the cellulose hydrogels, resulting in cellulose assembling precursor. The anchored cellulose matrix in the hydrogels restricts the strong H-bond interaction and causes the effect of steric hindrance which would prevent the rapid aggregation of cellulose in subsequent evaporation process. Therefore, ordered cellulose self-assemblies might be spontaneously formed during the slow dehydration of cellulose.

Relying on the above strategy in this study, two ordered structures, namely, high-aspect-ratio fibers and cellulose sheets, as well as the transitional states between them, have been observed. Furthermore, the ordered cellulose structures are employed to prepare 3D films of highly ordered structure and high strength. The study is expected to lay a foundation on fabricating ordered and high-strength cellulose materials. The study devotes to the investigation on the rules of cellulose self-assembling and the control mechanism of cellulose ordered structures. Meanwhile, we believe that the work would help to understand the deposition behavior and hierarchical alignment of cellulose in organisms.

2. Experimental

2.1. Chemicals and reagents

The high-purity cellulose, cotton linter pulp, is a gift from Yinying Chemical Firer Co. Ltd. (Gaomi, Shandong Province, China). The cellulose is of average polymerization degree of ~ 525 . NaOH and urea of analytical reagent grades are obtained from Shanghai Chemical Reagent Co. Ltd. *N,N'*-methylene bisacrylamide (MBA) is a product of Fuchen Chemical Reagents Factory (Tianjin China). All of them are used directly, without further purification.

2.2. Preparation of cellulose hydrogels in aqueous solvent media

At first, a 7 wt% NaOH/12 wt% urea aqueous solution is pre-cooled to -12°C , and then the weighted cotton linter pulp is added and stirred under the temperature of $0-4^{\circ}\text{C}$. After adequate dissolution of the cotton linter pulp for 5 min, the aqueous dispersion is centrifuged at 4000 rpm for 10 min to eliminate the small quantities of residual undissolved cellulose crystals and the suspending bubbles. Thereafter, a transparent aqueous solution of $\sim 3\%$ cellulose is obtained.

MBA powders of various known weights are directly added into different vessels of the above cellulose aqueous solutions at room temperature. An agitation of 30 min is needed to ensure homogeneous mixing between cellulose and MBA powder. The dispersions are left at room temperature for 4 h, during which the cloudy dispersions become transparent gradually. Finally, solid-like cross-link blocks (cellulose hydrogels) are formed, indicating that cellulose has been grafted with MBA.

In order to eliminate NaOH and urea encapsulated in cellulose hydrogels, the hydrogels are soaked in a large amount of deionized water for two days, which would be replaced by fresh deionized water frequently, until pH reaches ~ 7 . In that way, cellulose hydrogels rich in water are prepared.

2.3. Acquisition of cellulose self-assembly precursors

Cellulose self-assembly precursors are acquired by a top-down method. To be specific, 10 g cellulose hydrogels are shredded by ultrasonication in 0 or 100 mL of deionized water using Scinenz-IID ultrasound shredder (Scinenz Biotechnology Co., LTD, Ningbo, China) with a 6 mm probe at 60% amplitude for 2 min. In this way, each of cellulose hydrogels is smashed into a mass of small cellulose elements stably suspending in water, which is used as a self-assembly precursor subsequently.

2.4. Preparation of cellulose self-assemblies

Cellulose suspensions are freeze-dried to clearly determine the morphologies of cellulose self-assemblies. Here, cellulose suspensions are pre-cooled in advance in a refrigerator, and then transferred to a cold well of -50°C equipped with a vacuum-pumping device. After 12 h of freeze-drying, cellulose self-assemblies are formed.

2.5. Preparation of 3D cellulose films of highly ordered structure

3D cellulose films are prepared using a templating method. After homogeneous mixing between the aqueous solutions of 3% cellulose and MBA powders with $r=0.375$, 0.473, and 0.545, the dispersions are cast into cuboid glass grooves. Thus, rectangular cellulose hydrogel films are first obtained after 4 h of chemical cross-linkage. Afterwards, the hydrogel films are soaked in deionized water for 2 days to eliminate NaOH and urea. Finally, the hydrogel films are sandwiched between two parallel glasses

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