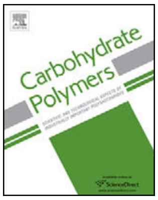
Carbohydrate Polymers 117 (2015) 408–413

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Facile fabrication of hierarchical cellulose nanospicules via hydrolytic hydrogenation

Kesavan Devarayan[b], Hak-Yong Kim[a,b], Byoung-Suhk Kim[a,b,*]

[a] *Department of Organic Materials & Fiber Engineering, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju-si 561-756, Jeollabuk-do, Republic of Korea*
[b] *Department of BIN Fusion Technology, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju-si 561-756, Jeollabuk-do, Republic of Korea*

ARTICLE INFO

Article history:
Received 4 September 2014
Received in revised form
22 September 2014
Accepted 3 October 2014
Available online 12 October 2014

Keywords:
Cellulose nanospicules
Hydrolytic hydrogenation
Hierarchical nanostructures
Electrospinning
Cellulose nanorods

ABSTRACT

A new spicule-like cellulose nanostructure is prepared from electrospun cellulose nanofibers using a one-pot bifunctional catalysis strategy namely hydrolytic hydrogenation. The electrospun cellulose nanofibers or cellulose film was treated in presence of catalyst consisting of an alkali and a metal to produce celluloses with structures like nanospicules, nanoflowers or nanorods, respectively. This work highlights the promising combination of electrospinning and hydrolysis/hydrogenation for facile production of hierarchical cellulose nanostructures such as nanospicules and nanorods.

1. Introduction

Polymers from renewable natural resources are very useful raw materials in day-to-day life. Among natural polymers, cellulose is the most abundant polysaccharide that constitutes approximately 1.5×10^{12} t of total biomass produced in a year (Klemm, Schmauder, & Heinze, 2002). The major sources are wood and plant, whereas tunicates, bacteria and algae are also known to produce cellulose (Moon, Martini, Nairn, Simonsen, & Youngblood, 2011). Traditionally, cellulose is used for two general purposes. On one hand, it has been used as a raw material for manufacturing of commodities such as paper, board, and textile fibers. On the other hand, it is utilized as a precursor to produce artificial cellulose-based threads and films by means of chemical conversions. The major attraction for research on cellulose is not only because of abundance and economy but also due to its unique structure combined with properties such as biocompatibility, hydrophilicity, and the presence of reactive hydroxyl groups, which allows introduction of new functionalities that are useful for several applications (Heinze & Liebert, 2001).

Nanofabrication technology is a potential tool to modify the properties of natural polymers for sustainable developments (Na et al., 2014; Yinjuan et al., 2013). In view of green chemistry principles, the interests in nanomaterials have shifted toward the use of cellulose in recent years. Cellulose itself is not ascertained as a highly performing material, while hierarchical nanostructures that compose of cellulose fibers opens up opportunities for a wide range of applications in technical textiles, medical industries, and separation techniques. Based on the morphology, nanocellulose is classified into three types namely (i) cellulose nanofibers, (ii) cellulose micro/nanofibrils, and (iii) cellulose micro/nanocrystals or cellulose nanowhiskers (Moon et al., 2011; TAPPI, 2012). Different methods have been developed in recent decades to produce these nanocellulosic materials by adopting mainly two principles, broadly known as physical and chemical modifications. In physical methods, the cellulose is subjected to mechanical processes such as ultrasonication (Johnson, Zink-Sharp, Renneckar, & Glasser, 2009; Wang & Cheng, 2009), high-pressure homogenization (Stelte & Sanadi, 2009; Turbak, Snyder, & Sandberg, 1983), grinding/crushing (Iwamoto, Nakagaito, & Yano, 2007; Chakraborty, Sain, & Kortschot, 2005), and/or microfluidization to produce micro/nanofibrillated cellulose. In the case of chemical method, the micro/nanocrystalline cellulose is produced by an acid hydrolysis treatment. Both techniques involve in pre-treatment, mostly TEMPO oxidation (Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006),

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* Corresponding author at: Department of Organic Materials and Fiber Engineering, Chonbuk National University, 567 Baekje-daero, Deokjin-gu, Jeonju 561-756, Republic of Korea. Tel.: +82 632702352; fax: +82 632702348.
E-mail addresses: kbsuhk@jbnu.ac.kr, kbsuhk@yahoo.com (B.-S. Kim).

http://dx.doi.org/10.1016/j.carbpol.2014.10.002
0144-8617/

followed by disintegration, deconstruction or depolymerization of the cellulose. Electrospinning is also the other versatile technique for production of electrospun non-woven mats of cellulose nanofibers (Cs-ESNWs) (Greiner & Wendorff, 2007).

Inspired by the hydrogen formation in alkaline corrosion reactions of aluminium, in this study, a novel strategy combining electrospinning and hydrolytic hydrogenation is used to produce unique cellulose nanospicules. To the best of our knowledge, for the first time, herein we introduce a new type of nanocellulose consisting of spicule-like nanostructures obtained by in situ hydrolysis/hydrogenation technique. Hydrolytic hydrogenation has become a widespread technique until recently after successful catalytic conversion of polysaccharides into low molecular weight saccharides. Hydrolytic hydrogenation is a bifunctional catalytic strategy consisting of a transition metal catalyst and a dilute acid or an acidic solid support (Vyver, Geboers, Jacobs, & Sels, 2011). For the first time, we demonstrate hydrolytic hydrogenation of cellulose using weak alkaline solution. By effectively controlling the hydrolysis/hydrogenation of electrospun cellulose nanofiber mats and films, new cellulose nanostructures were produced in this study.

2. Experimental

2.1. Electrospinning

The solution of cellulose acetate (CA, $M_n = 50{,}000$ g/mol, Aldrich) was prepared using dimethylacetamide/acetone (volume ratio = 1:2) at the concentration of 7–8 wt%. The solution was placed in a 10-mL syringe attached to a plastic tip with an inner diameter of 0.6 mm. The electrospinning was carried out at 9.5 kV (NanoNC power supply, Republic of Korea) at a tip-to-collector distance of 18 cm at about 25 °C and relative humidity of 45–50%. The electrospun fibers were collected on a grounded aluminium foil followed by drying at 25 °C in vacuum for 24 h and then stored at room temperature until further use (Khatri, Wei, Kim, & Kim, 2012; Kim & Kim, 2011).

2.2. Preparation of cellulose nanostructures

At first, the CA electrospun non-woven (CA-ESNW) mat collected on an aluminium foil was cut into small pieces (ca. 4 × 5 cm). Secondly, a set of CA-ESNW mats were peeled-off and deacetylated in 0.05 M NaOH solution for 24 h at 25 °C to regenerate cellulose nanofibers (*P-Cs-ESNWs*) (Liu & Hsieh, 2002). Another set of CA-ESNW mats with aluminium foil were treated in 20 mL of aqueous alkaline solutions having 0.05 M, 0.1 M, 0.5 M, and 1.0 M of NaOH at ambient conditions. After a specific treatment time (1.5 min, 3 min, and 5 min), the aluminium foil was removed from the alkaline solution and further continued the treatment of CA-ESNW in alkaline solution for another 24 h under mechanical shaking in order to obtain regenerated cellulose fibers. Then the cellulose nanofiber mats were washed with distilled water for at least 3 times at the interval of 5 h followed by drying in vacuum for 24 h at 25 °C to obtain *H-Cs-ESNWs*. On the other hand, CA films were cast on aluminium foil using 7 wt% of CA solution followed by drying in vacuum for 24 h at 25 °C. The films were treated in alkaline solutions similar to the CA nanofiber mats. The mean thickness of the resulting cellulose fibers and film were measured as 70 and 10 μm, respectively, using a digital micrometer (Mitutoyo ABSOLUTE) with a resolution of 1 μm.

2.3. Characterization

Scanning electron microscopy (SEM) images were taken using a JEOL JSM-5900 scanning electron microscope after sputtering the samples with platinum for 120 s. Energy dispersive X-ray measurements were conducted using the EDAX system attached to the same microscope. A field-emission microscope (FE-SEM) was also used to observe the morphologies after sputtering the samples with osmium for 7 s. X-ray diffraction (XRD) patterns were recorded on a Rikaku X-ray diffractometer (Cu $K\alpha$ radiation).

A CA-ESNW mat was hydrolysis/hydrogenated in 1.0 M NaOH. After 10 min the nanofiber mat was completely solubilized in 1.0 M NaOH. Then the solution was neutralized using 1.0 M HCl and the fragments were analyzed by Fourier-transform infrared spectroscopy (FT-IR, Perkin Elmer) and liquid chromatography–mass spectrometry (LC/MS spectrometer, Agilent 1100 LC/MS).

3. Results and discussion

Two sets of experiments were carried out for the preparation of hierarchical cellulose nanostructures. In the first experiment, the alkali treatment of cellulose acetate (CA) nanofibers that were electrospun on aluminium foil was investigated. On one hand, the CA-ESNW nanofiber mats were peeled-off (P) from the aluminium foil and deacetylated in 0.05 M NaOH solution (Fig. 1a) to regenerate the cellulose-nanofibers (Cs-ESNW). These regenerated cellulose nanofiber mats were indicated by *P-Cs-ESNW*. On the other hand, the CA nanofibers on aluminium foil were directly treated in aqueous NaOH solutions of varying concentrations (0.05–1.0 M NaOH) for a relatively short time ranging from 1.5 to 3 min. These samples were indicated by *H-Cs-ESNWs*. Fig. 1b–d shows the morphological changes in regenerated cellulose fibers upon treatment with alkaline solution. With very low concentration of NaOH and short treatment time, for instance, 0.05 M NaOH and 3.0 min, the cellulose fibers developed a spicule-like nanostructure. Fig. 1d shows the magnified FE-SEM image of cellulose nanofibers with spicule-like nanostructures. It clearly reveals that parts of the cellulose nanofibers split into spicules that still stuck on the originating fiber surface. Furthermore, X-ray diffraction (XRD) patterns of *H-Cs-ESNW* and *P-Cs-ESNWs* exhibited peaks at $2\theta = 20.3^\circ$ and 22.7° corresponding to (4.31 Å) and (3.94 Å) d-spacing, which are characteristics of cellulose I structure (Fig. 2) (Nishiyama, Langan, & Chanzy, 2002; Teixeira et al., 2010). The XRD results revealed that the ordered structure of the crystalline region on the *H-Cs-ESNW* is not disrupted by hydrolysis/hydrogenation. In other words, spicule-like crystalline nanostructures can be produced via a simple hydrolysis/hydrogenation technique.

At about 3.0 min of alkaline treatment in 0.05 M NaOH, the fiber mats get detached from the aluminium foil due to rapid evolution of hydrogen gas. Meanwhile, increase in the alkaline strength from 0.05 to 0.1 and 0.5 M NaOH indicated the development of a non-homogeneous flower-like nanostructure in the cellulose fibers (Fig. 3a). Further increase in the concentration of alkali has led to the dissolution of cellulose fibers as seen in Fig. 3b. For the ease of understanding, the splitting up of cellulose nanofibers into spicule-like nanostructure can be compared to the blossoming of a bud to a flower, where one edge of the petal are attached to the stem of the flower.

The anomalous behavior of cellulose fibers in presence of aluminium and NaOH can be explained by means of hydrolysis/hydrogenation mechanism. Aluminium is readily corroded in alkaline environment even at room temperature. The combination of aluminium/aqueous NaOH is a well-known system for hydrogen production (Belitskus, 1970; Soler, Candela, Macanás, Muûoz, & Casado, 2009; Martíneza, Benítesa, Gallegosa, & Sebastiàn, 2005) and is represented by the following series of reactions.

$$2Al + 6H_2O + 2NaOH \rightarrow 2NaAl(OH)_4 + 3H_2 \quad (1)$$