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Isolation and characterization of cellulose nanocrystals from garlic skin

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ABSTRACT

For the value-added utilization of underutilized agricultural by-products, garlic skin obtained abundantly in the food processing industry has been tested as a new source of cellulosic materials. Cellulose microfibers (CMF) and cellulose nanocrystals (CNC) were isolated from garlic skin fibers by alkali treatment and acid hydrolysis. The crude fiber, CMF, and CNC of garlic skin were characterized by Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and Transmission electron microscopy (TEM). Most of the lignin and hemicellulose was removed after the chemical treatment, and the degree of crystallinity of the CMF and CNC was increased compared with the crude fiber. The degree of crystallinity was 35%, 45%, and 63% for the crude fiber, CMF, and CNC, respectively. The cellulose nanocrystals exhibited spherical in shape with the size of 58–96 nm. The thermal stability of the CMF increased significantly, but that of CNC decreased slightly due to the introduction of sulfate groups into the cellulose crystals during acid hydrolysis. The nanocrystals had a high potential to be used as reinforcing filler for the preparation of bionanocomposites.

1. Introduction

The search for new renewable resources for the production of biodegradable and biocompatible materials has steadily increased in recent years [1]. In particular, non-conventional sources of cellulosic fibers have been extensively studied. There are various unexplored valuable cellulosic materials in the agricultural and food processing industry obtained as waste or by-products. These non-conventional and underexploited renewable materials can be used as an interesting alternative to produce value-added biopolymeric materials such as preparation of cellulose nanofibers and other uses [2]. Various agricultural residues and nonwood fibers generated from forestry or agri-food industries have been used to extract cellulose nanofibers, whiskers, and nanocrystals for the value-added utilization [3]. Among such underutilized cellulose resources, garlic skin is one of the promising materials. Garlic (*Allium sativum* L.) has been widely used due to its culinary and medicinal attributes in various regions of the world such as Asia, the Middle East, northern Africa, southern Europe, and parts of South and Central America. The garlic consumption in 2010 was estimated for 2.3 pounds per person [4]. Accordingly, tremendous amount of garlic skin is expected to be discarded as a processing waste in the food processing industry, especially for the production of minimally processed deskinned garlic. Garlic skin has already been used for fruits and vegetable coatings [5], extraction of antioxidants [6] and for removal of Cu^{2+} from the aqueous stream [7].Surface topography and roughness of garlic skin have been studied by atomic force microscopy in order to estimate the surface area for the coating purpose [8]. However, to the best of our knowledge, garlic skin has not been used as a new source of cellulose materials for the production of cellulose micro- and nanofibers.

Therefore, the main objective of the present work were extraction and characterization of cellulose micro-fibers and cellulose nanocrystals from garlic skins in order to test their potential for the value- added utilization as a new source of cellulosic fiber materials.

2. Materials and methods

Materials: Garlic skin was obtained from a local food processing company. Sodium chlorite, sodium bisulfate, sulfuric acid and ethanol were purchased from Sigma Aldrich (St Louis, MO, USA).

Chemical analysis and isolation of cellulose nanocrystals: Garlic skin was washed thoroughly with water to remove dirt and dried in an air oven at 100 °C for 24 h. The dried samples were ground into fine powder using a Waring blender, and used for further analysis and extraction of cellulose microfibers (CMF).

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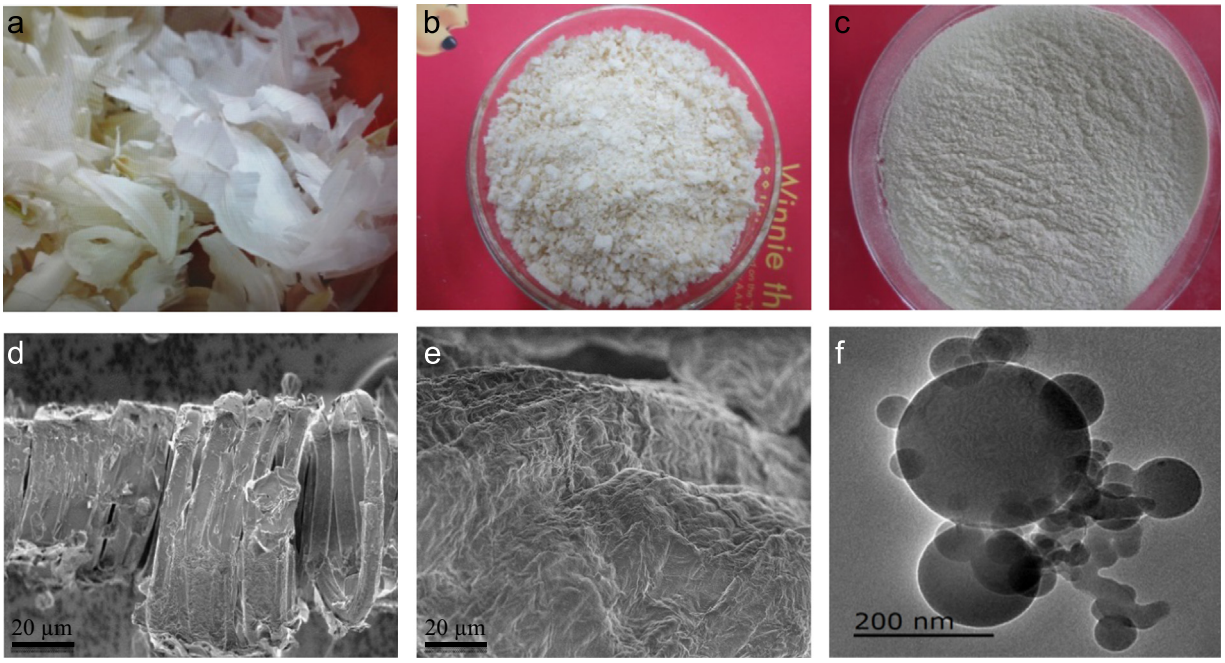

Fig. 1. Apparent shapes of (a) garlic skin, (b) CMF, and (c) CNC; SEM images of (d) crude fiber and (e) CMF; TEM image of (f) CNC.

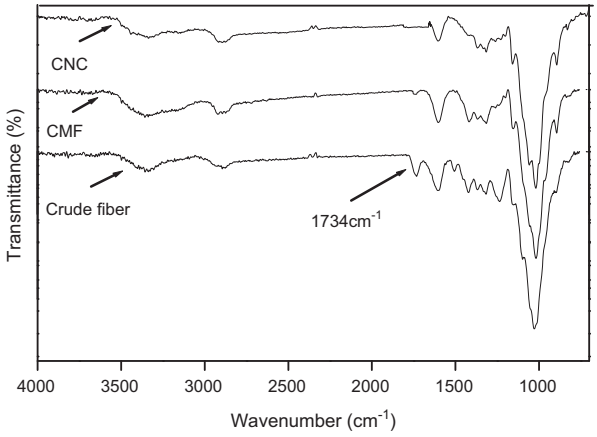

Fig. 2. FT-IR spectra of garlic skin fiber and its CMF and CNC.

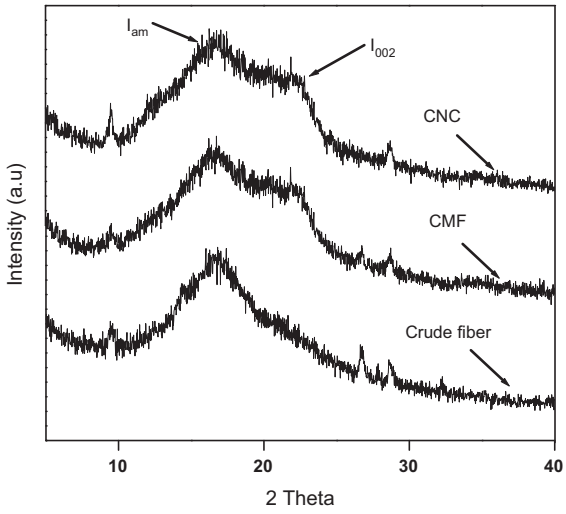

Fig. 3. XRD patterns of garlic skin fiber and its CMF and CNC.

The contents of α-cellulose, hemicelluloses and lignin of the garlic skin fiber were determined according to the methods of quantitative analysis of grass fibers [9,10]. The CMF was extracted from the crude fiber of garlic skin by alkaline extraction, and the cellulose nanocrystal (CNC) was isolated from the CMF by acid hydrolysis [10]. For this, 5 g of CMF was hydrolyzed by refluxing with sulfuric acid (45% H_2SO_4 with fiber to liquor ratio of 1:20) for 2 h at 60 °C with strong agitation. Hydrolysis was quenched by adding an excess of distilled water to the reaction mixture and the resulting mixture was cooled to room temperature. Then, the suspension was repeatedly centrifuged at 4000 rpm for 20 min using a centrifuge (Hanil Scientific Centrifuge, Incheon, Kyunggido, Korea) and the supernatant was discarded until it became turbid. The suspension was then sonicated using an ultrasonifier (Sonics, SUS-304, Jeonyoung Co., Ltd. Chungnam, Korea) for 5 min in an ice bath. The suspension was then subjected to dialysis with distilled water until neutrality was attained, then it was freeze-dried to get dried CNC.

Characterization: FT-IR spectra of fiber samples were obtained using an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrophotometer (TENSOR 37 Spectrophotometer with OPUS 6.0 software, Billerica, MA, USA) in the range of 4000–500 cm^{-1}.

X-ray diffraction patterns of CNF obtained from garlic skin fiber was tested using a XRD diffractometer (PANalytical Xpert Pro XRD diffractometer, Amsterdam, Netherlands). It was scanned in the range of $2\theta = 5–50^{\circ}$ with a scanning rate of 0.4°/min at room temperature. The crystallinity index (CrI) was calculated using the following equation [11]:

$$CrI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

where I_{002} is the intensity of the 002 peak (at $2\theta = 22^{\circ}$) and I_{am} is the intensity of the peak at $2\theta = 16^{\circ}$.

The thermal stability of the fiber samples was tested with thermogravimetric analyzer (TGA/DSC 1, Mettler Toledo, Schwarzenbach, Switzerland). About 5 mg of each sample was heated from room temperature to 600 °C at a heating rate of 10 °C/min under a nitrogen flow rate of 50 cm^3/min.