Extraction of thermally stable cellulose nanocrystals in short processing time from waste newspaper by conventional acid hydrolysis

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Abstract
Motivated by many exclusive and useful features of cellulose nanocrystals (CNC) and the underutilized resource of waste newspaper, this study aimed to extract CNC from waste newspapers by means of alkali and bleaching treatments followed by acid hydrolysis. The morphological structure of the obtained CNC was analysed by optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) methods. The remarkable removal of surface contamination and the reduction in fiber diameter during alkali and bleaching treatment were observed and the nano-dimension of the extracted CNC was revealed with the average diameter of 12.3 ± 2.8 nm. Characterization of the extracted CNC showed a high whiteness index of 80%, and high transparency of about 80% of the light at 600 nm calculated for a 0.02 mm thick nanocellulose film. Fourier transform infrared spectroscopy (FTIR) indicated that lignin, hemicellulose and other coloring agents were successfully removed. A comparably high crystallinity index of 80.15% was calculated from x-ray diffraction data. Thermogravimetric analysis showed that the product had a typical maximum thermal degradation at 300 °C. The analysis results indicated the successful extraction of good CNC from waste newspaper with the shortest processing time ever reported for acid hydrolysis with conventional alkali and bleaching pretreatment. The findings also strongly support for further research of nanocomposites reinforced by CNC produced from waste newspaper.

1. Introduction

Cellulose, one of the most abundant polysaccharide polymers, has versatile uses in many industries such as veterinary foods, wood and paper, fibers and clothes, cosmetic and pharmaceutical industries. Cellulose consists of both amorphous and crystalline structure. Cellulose nanocrystals (CNC) are produced by removing the amorphous cellulose and fragmentation of cellulose fibers. Due to the unique properties of CNC such as low density, biodegradability, high aspect ratio, high strength and stiffness, CNC have become an attractive and ideal material for various potential applications [1, 2]. For example, CNC can be used as biomedical material [3, 4], gel nanomaterial [5], polymer nanocomposite [6], and polymer electrolyte [7].

Recently, CNC have been widely produced from various sources such as jute, sisal, cotton, ramie, tunicate, bacteria and wood pulps. Beside these sources, wastepaper which is also a cellulose biomass could be considered as an underutilized but promising source for CNC production [8]. According to the survey about pulp and paper capacity conducted by FAO in 2017–2022, the total capacity of paper and paperboard in 30 countries that participated in the survey was 261.201 million tons in 2019 and the expected capacity in 2022 will be 267.048
million tons [9]. Particularly, the capacity of newsprint from those countries in 2019 was 15,146 million tons and will reach 15,311 million tons in 2022. With the huge amount of newsprint production and limited ratio of paper-to-paper recycling, waste newspaper could be a potential source for CNC production.

In the effort of waste newspaper utilization for CNC extraction, some preliminary results have been reported. CNC were extracted by boiling the material for more than 12 h, reboiling the resulting pulp after subjecting it to alkali treatment (5% (w/v) NaOH), and applying bleaching treatments (2% (v/v) NaClO) followed by controlled-condition of acid hydrolysis (60% (v/v) H2SO4 solution at 45 °C for 1 h) [10]. The CNC were successfully isolated with a crystallinity index of 75.9%. A similar approach without boiling raw material in water was applied to extract CNC from non-printed recycled newspaper by applying an alkali treatment with 5 wt% NaOH via initial homogenous mixing before boiling the mixture at 125 °C for 2 h under continuous stirring, followed by a repeated bleaching treatment with 2% (w/v) NaClO2 at 125 °C for other 2 h until the white sample was obtained. It was reported that the extracted CNC had a higher crystallinity index of 90.1%, which might be the result of using non-printed area of recycle newspaper as the raw material [11]. In contrast, CNC isolation could also be performed by direct acid hydrolysis (60% (v/v) H2SO4 solution at 45 °C for 1.5 h) without the alkali and bleaching pretreatment. However, the first maximum degradation temperature of the CNC product was at 220 °C [12], which was relatively lower than most reported temperature of about 300 °C [8, 13–15]. It was highly probable that direct and longer process of acid hydrolysis could have degraded the thermal stability of the CNC product [16].

Because CNC is often regarded as a potential candidate to produce strong natural fibre-reinforced thermoplastic composites, thermal stability of CNC is one of the major properties to be considered [17]. However, the thermal behavior of CNC has a large variation, depending on the source and the chemical treatment of the raw material. To obtain CNC with good thermal stability from old newspaper, this study followed the acid hydrolysis approach with two-step pretreatment based on previous studies [10–12]. More importantly, this study proposed a shorter CNC extraction process, with a marginal processing time for pretreatment of raw material and acid hydrolysis of the pretreated pulp.

The morphological structure analysis and visual inspection (i.e., whiteness index) of the extracted CNC were performed on images captured using optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). In addition, characterization of the product was carried out by using Fourier transform infrared spectroscopy (FTIR) for chemical analysis, x-ray diffraction (XRD) for crystallinity index calculation, thermogravimetric analysis (TGA) for thermal stability analysis, and UV–Vis spectrophotometer for visual light transmittance of the obtained CNC.

2. Material and methods

2.1. Material
Waste newspapers that contained inks were collected in Can Tho City, Vietnam and were used as the cellulose source. Sodium hydroxide (96%), sodium hypochlorite (8.4%), sulfuric acid (99.9%), and acetic acid (99.95%) were purchased from Xilong Scientific Co., Ltd., China, and used without any further purification.

2.2. Methods
2.2.1. Extraction of cellulose from waste newspaper
The alkali treatment was designed to solubilize embedded hemicellulose residuals and any other extracts in raw materials by reducing the intermolecular hydrogen bonding and others. Small newspaper pieces of 1 × 1 cm were ground and alkali-treated. Specifically, 5 g of ground newspapers were added to 300 mL of 2 wt% NaOH solution at 100 °C in an optimum time of 3 h under continuous stirring. Then the sample was rinsed with water until pH = 7. The bleaching was conducted by adding 5 g of ground newspaper to 300 mL of 2 wt% NaClO solution at 70 °C in an optimum time of 1 h under continuous stirring. During the process, 5 mL of acetic acid (CH3COOH) solution was added dropwise into the mixture. Then the sample was rinsed with water until pH = 7.

2.2.2. Isolation of cellulose nanocrystals
CNC were isolated by acid hydrolysis using sulfuric acid in a similar preparation flow as reported in [11, 18]. An amount of 50 mL of 64 wt% H2SO4 was dropwise added into 5 g of the previously prepared cellulose. Then the mixture was continuously stirred and heated in 45 min, which was found to be optimum, at 45 °C. The reaction was terminated by adding 1 L of distilled water. The final product was neutralized by rinsing with water.

Table 1 shows a comparison of the required time for all main preparation and processes in this study and previous studies using newspaper as the raw material for CNC extraction. It was obvious that the proposed method with two-step chemical pretreatment and acid hydrolysis had the minimum CNC extraction time.
Table 1. Required time for critical processes and preparation for CNC extraction.

| References            | Alkali treatment | Bleaching treatment | Acid hydrolysis | Minimum time for critical processes and preparation |
|-----------------------|------------------|---------------------|-----------------|---------------------------------------------------|
| This study            | 3 h              | 1 h                 | 0.75 h          | 4.75 h                                            |
| Danial et al 2015 [10]| >12 h (boiling)  | Unreported          | 1 h             | >13 h                                             |
|                       | + unreported reboiling time |                   |                 |                                                   |
| Mohamed et al 2015 [11]| Unreported time for solution homogenization | 2 h              | 1 h             | >5.0 h                                            |
|                       | + 2 h            |                     |                 |                                                   |

+ time for repeated process until a white sample was obtained
2.2.3. Determination of cellulose composition
The cellulose content of the raw newspaper and chemically treated fibers was determined by applying TAPPI 203-99. Table 2 shows the average cellulose content of the three tested samples.

| Sample                  | Cellulose content (%) |
|-------------------------|------------------------|
| Raw newspaper           | 88.66                  |
| NaOH treated fiber      | 93.47                  |
| NaClO treated fiber     | 97.45                  |

2.2.4. Morphological structure analysis
The morphology of the raw newspaper and chemically treated fibers was firstly observed by using an optical microscope (Nikon, ECLIPSE LV100POL, Japan), which was equipped with an autofocusing module to obtain the All-In-Focus image for better visibility of the product. The detailed surface morphology of samples was observed by using SEM (Jeol/ JSM-6480LV Japan). The dimensions of the fiber after acid hydrolysis were obtained by using TEM (Microtrac S3500, USA). In addition, GNU Image Manipulation Program was applied to determine the average diameter of the product.

2.2.5. Fourier transform infrared spectroscopy
Fourier transform infrared spectra were obtained by using FTIR (ATR—FTIR 4700, Jasco, Japan) for analysing the raw newspaper and chemically treated fibers.

2.2.6. X-ray diffraction
The crystalline structure of BHET was verified by XRD (RINT2500, Rigaku, USA). The diffracted intensity was measured by scanning a range of $2\theta = 5^\circ$–$50^\circ$. The crystalline index-to-amorphous ratio for the final product were determined as

$$\text{Cr.I} = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%$$

(1)

2.2.7. Thermogravimetric analysis
Thermogravimetric analysis (TGA) of the product was conducted by Discovery TGA (TA Instruments) with heating rate of 20 °C min$^{-1}$, at temperature from 20 to 700 °C.

2.2.8. Whiteness determination
In this study, the whiteness level of the CNC product was determined based on image processing using MATLAB. A small amount of CNC product was put on a white calibration target. The captured RGB image $I_{RGB}$ of the product was converted into a gray image $I_{gray}$ whose histogram-equalized version $I_w$ was obtained for whiteness level determination.

To determine the region of the CNC in the image, binary thresholding was applied on the blue channel of image $I_{RGB}$ due to its high contrast. The expected outcome of this binary thresholding was the image mask $I_m$ such that a pixel that belonged to the nanocellulose product and the background region would receive the value 1 and 0, respectively. The whiteness index of the CNC product was determined in the range of [0, 100%] as

$$\text{whiteness_index} = \frac{1}{255} \sum_{x,y} I_w(x, y) \ast I_m(x, y) \times 100\%$$

(2)

where $N$ is the total number of white pixels in $I_w$ and $(x, y)$ is the pixel coordinate.

2.2.9. Transmittance determination
Transmittance under visible light of the obtained CNC were evaluated by measuring the transmittance with UV–vis spectrophotometer (6800 UV/Vis, Jenway).
3. Results and discussion

3.1. Morphological structure analysis and visual inspection

Figure 1 shows the difference in color of the raw material and chemically treated fibers. After alkali treatment, the color of the raw material changed from light grey (figure 1(a)) to light yellow (figure 1(b)) which was resulted from the presence of lignin in the alkali-treated product. Thus, it was necessary for further bleaching treatment of the product with NaClO solution in the presence of acetic acid ($\text{CH}_3\text{COOH}$) as proton donor to oxidize the chromophoric groups in lignin and to remove the by-products of such oxidation. As a result, the bleached fibers were observed with a certain level of whiteness (figure 1(c)), and the CNC were isolated with apparently higher whiteness level (figure 1(d)). In this study, a whiteness index was formulated to reflect the removal of lignin and other coloring agents during cellulose extraction and CNC isolation processes. The whiteness index values of raw material and the treated fibers were calculated using (1) and illustrated in figure 2. It was obvious that the obtained CNC had a higher whiteness index of 80%, which was remarkably high for CNC that was obtained from waste newspaper compared with those obtained from natural sources of material with the highest degree of whiteness up to 85% \cite{20, 21}.

For a preliminary analysis of the morphology of the fibers, their best-focused microscopic image was obtained by using an integrated autofocusing module that was developed on the principle of All-In-Focus algorithm \cite{22}. It was obvious that the diameter of the fibers were reduced after two-step pretreatment (figures 3(a)–(c)). Significant changes in surface and diameter of the fibers could be clearly observed in the SEM images of the fibers (figures 4(a)–(c)). Surface contamination was remarkably reduced. In addition, the diameter reduction of the fibers was confirmed and agreed with previous reports \cite{11, 23}.

The morphology of the obtained CNC was analysed using its TEM image (figure 5). CNC of rod shapes were observed although some aggregated zones of CNC dispersed in water were unavoidably captured due to sample preparation for TEM observation. Calculation of the diameter of the obtained CNC rods was performed by
Figure 3. Best-focused microscopic images of (a) raw materials; (b) alkali-treated fibers; (c) bleaching treated fibers.

Figure 4. SEM images of: (a) raw materials; (b) alkali-treated fibers; (c) bleaching treated fibers.

Figure 5. TEM image of CNC isolated from waste newspapers.
using a free and open source image manipulation program GIMP (ver. 2) [24]. The average diameter was 12.3 ± 2.8 nm, an acceptable value in comparison with those in previous reports [10, 17, 19, 23, 25].

3.2. FTIR spectroscopy analysis

The FTIR spectra of the raw material and chemically treated fibers are presented in figure 6. The most distinctive absorption peaks of the FTIR spectra of the raw fibers and the chemically treated fibers were observed at the wavenumbers of 1595, 1505, 1247 cm⁻¹, associating with the characteristics of lignin [11, 26, 27]. After alkali treatment, the small shoulder at 1595 cm⁻¹ corresponding to the C= C unsaturated linkages and aromatic rings in lignin was not present. Small peaks at 1505, 1247 cm⁻¹ corresponding to the aromatic C= C in plane symmetrical stretching vibration in lignin and C–O of the guaiacyl unit stretching vibration in lignin became less significant after alkali treatment and were insignificant after bleaching treatment. The peak at 1247 cm⁻¹ also indicated the acyl-oxygen CO–OR stretching vibration in hemicellulose. No peak was observed in the region of 1728–1731 cm⁻¹, which was reported as the characteristics of hemicellulose [23]. In addition, no peak was observed at 897 cm⁻¹, which is considered as the ’amorphous band’ after acid hydrolysis [13].

Figure 6. FTIR spectra of waste newspaper, NaOH treated, NaClO treated fibers and CNC.

The peaks at 1430 cm⁻¹ which correspond to –CH₂ bending vibration, a typical of the ’crystallinity band’ in cellulose were also found [13]. The peaks in the 3333–3500 cm⁻¹ and 1610–1639 cm⁻¹ regions indicated the presence of O–H stretching vibration and O–H bending of the absorbed water, respectively. The observed intensity increase at peak 1635 cm⁻¹ in FTIR spectra of the obtained CNC might be due to the cellulose-water interaction [28].

The peaks observed at 2360 and 2340 cm⁻¹ signified the presence of C=O [29] resulting from CO₂ adsorption of cellulose from the normal atmosphere whose mechanism could be explained mostly by Lewis acid-base interaction [30]. The observed intensity increase at peaks 2360 and 2340 cm⁻¹ of the obtained CNC might be due to the increase in the surface area of CNC and the strong CNC-water interaction that facilitated CO₂ adsorption [31]. This well-known specific property of CNC led to the application of nanocellulose-based membranes for CO₂ capture [32].

3.3. XRD analysis

Figure 7 shows the XRD diffraction pattern of the CNC product with the diffraction peaks at 2θ = 14.8°, 22.5°, and 34.32°, which were very close to the typical peaks of cellulose crystal structures reported in [11, 13, 27, 28, 33]. Sharp and narrow diffraction peak at 2θ = 22.5° indicated high perfection of the crystal lattice. The crystallinity index calculated by (2) was 80.15% which was higher than reported value in previous studies [10, 17, 19, 23].

3.4. Thermogravimetric analysis

The TG and derivative thermo gravimetric (DTG) curves of the extracted CNC were shown in figure 8. A small weight loss (about 7 wt%) was found in the range of 30 °C–150 °C due to the evaporation of the humidity of the material or low molecular weight compounds remaining from the isolation procedures. This weight loss was reported to be linked to the scission of glycosidic bonds, leading to a reduction in the degree of polymerization of
cellulose without losing any mass [17]. No weight loss was observed at the temperature range of 160 °C–250 °C that can indicate of hemicellulose depolymerization [34]. The onset decomposition temperature and the temperature at the maximum weight loss of CNC were 270 °C and 300 °C, respectively with the weight loss of 45.5 wt%. The peak at 300 °C which were in line with the previous report [19, 35] could be related to the dehydration of cellulose to dehydrocellulose [36, 37]. A small broadening or shoulder on the right side of the main peak at about 380 °C could be due to a broad distribution of molecular mass of isolated cellulose or the depolymerization of cellulose in competition with dehydration. The solid residue at 600 °C was 25.6 wt%.

Table 3 shows a comparison of CNC products reported in studies that performed CNC isolation from waste newspaper by acid hydrolysis with alkali and bleach pretreatment. It was obvious that CNC with higher crystallinity index (up to 90.15%) could be extracted from non-printed areas of newspaper (i.e. recycled newsprint without ink), which was also reported by other CNC extraction method [12]. However, the obtained CNC had a relatively high crystallinity index of 80.15%, and remarkably better thermal stability with the first maximum thermal degradation at 300 °C which might be partly due to the optimum duration of acid hydrolysis. With the optimum duration of acid hydrolysis, less sulfate groups on nanocrystals resulted in higher maximum degradation temperature. In addition, the thermal stability of the CNC product was improved by its crystalline regions [38, 39].
3.5. Transmittance under visible light

Light transmittance spectra of nanocellulose films with various thickness was shown in figure 9. It was observed that 0.02 to 0.09 mm thick films were transparent under visible light. Particularly, 0.02 mm thick films transmitted about 80% of the light at 600 nm. The transmittance tended to reduce due to the increase in the film thickness. The transmittance of 0.09 mm thick films was about 66% of 600 nm light. High transparency was a remarkable feature of the obtained CNC.

4. Conclusions

CNC were successfully produced from waste newspaper by acid hydrolysis with alkali and bleaching pretreatment. Morphological analysis using SEM and TEM images of the CNC product demonstrated its rod-like structure with an acceptable diameter of 12.3 ± 2.8 nm. FTIR analysis showed insignificant presence of hemicellulose and the amorphous state of cellulose. Thermogravimetric analysis results showed that the first maximum degradation temperature of the obtained CNC was at 300 °C. This indicated that the thermal stability was inconsiderably affected by dehydration reaction caused by the sulphate groups from the acid hydrolysis. This might be the result of the pretreatment and the optimum experimental conditions, especially the comparably shorter reaction time for the acid hydrolysis.

With a high degree of whiteness index of 80% and crystallinity index of 80.15%, the obtained CNC could be considered to have the highest whiteness and crystallinity index ever reported for CNC that were extracted from waste newspaper in the shortest processing time by acid hydrolysis with chemical pretreatment. The findings showed a strong support for the on-going research of nanocomposites reinforced by extracted CNC from waste newspapers.

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