ECO- AND AQUA-FRIENDLY NANO CRYSTALLINE CELLULOSE PREPARATION UNDER DEEP EUTECTIC SOLVENT

Hee Jin Kim,[1] Hye Kyung Kim,[2] and Hyung-Min Choi[1]
[1] *Dept.of Organic Materials and Fiber Engineering, Soongsil University, Seoul, Republic of Korea 06978*
[2] *Dept. of Fashion Design and Apparel Industry, Wonkwang University, Jeonbuk, Republic of Korea 54538*
hchoi@ssu.ac.kr

ABSTRACT

Water soluble esterified nanocellulose (ENC) was prepared with various anhydrides in expeditious, yet eco-friendly ways by using deep eutectic solvent (DES), ultrasonic and microwave irradiation. Phthalic anhydride and DES made of oxalic acid and choline chloride were mainly used as a reagent and solvent. Results indicated that shape and size of ENC could be varied by preparation methods. Analyses of ENC suggested that oxalic acid participated as both solvent and reactant, forming various types of anhydrides with reagent and cellulose. Characterization of ENC was performed by various instruments such as FTIR, TGA, X-ray diffraction, SEM, and zeta potential analyzer.

Key Words: nanocellulose, esterification, deep eutectic solvent, ultrasound, microwave irradiation

1. INTRODUCTION

Nanocellulose has been applied to numerous end-use applications such as reinforced composite materials, aerogel, film, etc. [1, 2]. The nanocellulose could be prepared by physical and chemical methods. Physical method employed ultrasonic and ultra-high pressure disperser, whereas chemical methods mainly used hydrolysis reaction by strong inorganic acid or enzymes and microorganisms [2]. The former was relatively simple, but requiring a large amount of energy and thus chemical method was often used to produce nanocellulose. Nevertheless, chemical method also showed certain limitations such as potential high toxicity, corrosion of equipment due to use of strong inorganic acid, high toxic effluent problem, long process time, etc. [3]. Therefore, the research must be continued for producing nanocellulose in more efficient and eco-friendly way.

One of the most important eco-friendly options in chemical processes is to replace volatile organic solvent by nonvolatile solvent such as deep eutectic solvent (DES). DES is composed of hydrogen donor and hydrogen acceptor [4, 5]. Hydrogen donors include amides, acids, and alcohols whereas hydrogen acceptor was mainly based on choline chloride. DES prepared by mixing hydrogen donor and acceptor showed great level of freezing point depression along with low vapor pressure, low toxicity, low cost, simple preparation, and high electric conductivity [5]. It was shown that DES was especially suitable in processing under microwave irradiation due to its high electric conductivity [6, 7]. In addition, use of ultrasound could also facilitate the process of materials by DES [3].

Aqueous system has certain advantages such as less toxicity, low volatility and low cost, but the reaction generally occurs in heterogeneous state due to water insolubility of cellulose caused by strong inter- or intra-chain hydrogen bonds [8]. Therefore, water-soluble cellulose derivatives have been developed. These derivatives commonly contained ether group such as sodium carboxymethyl cellulose and hydroxyethylcellulose, but other functional groups such as ester, sulfate, and phosphate could also be possible [8, 9]. These derivatives could find a large number of applications in various formulations including film forming, water-binding, lubricating, thickening, and gelling agents in many different fields such as agriculture, food, cosmetics, coating, oil industry, paper, textiles, pharmaceutical, etc. [9]. However, literature survey indicated that little study was carried out in formation of water soluble nanocellulose in eco-friendly ways.

Therefore, in this study water-soluble nanocellulose was prepared by applying common ester-forming reagents in DES. Microwave and ultrasound irradiations were employed to expedite the formation of nanocellulose in energy efficient and eco-friendly ways. As a representative DES, oxalic acid-choline chloride (OXC) was used as a DES system.

2. MATERIALS AND METHOD

2.1 Materials

Cellulose powder (Sigma C6288-250G, cellulose fiber medium) was obtained from Aldrich-Sigma, Inc., Korea. Other chemicals such as oxalic acid dehydrate (OA), choline chloride (ChCl), phthalic anhydride (PA), maleic anhydride (MA), and succinic anhydride (SA) were purchased from Daejung Chemicals, Korea. All the chemicals were reagent grades and used without further purification.

2.2. ENC Preparation

DES preparation has been described in the previous studies [4]. OA and ChCl at 1:1 mole ratio was stirred for one hour at 100°C until obtaining a transparent liquid (this DES was hereinafter expressed as OAC). A six gram of cellulose powder was placed in the beaker containing 50mL of OAC along with appropriate amounts of anhydride. The mixture was treated by ultrasonic sonicator (ULH-700S, Sonosmasher, Korea) at 19.85KHz and 700W for specific time. After a screening study, microwave irradiation was set up to 90 seconds by commercial microwave oven (MWO-20EC3, SK magic, Korea, 700W). The nanocellulose produced was washed by 1wt% of aqueous NaOH solution to remove acidic OAC and filtered twice to obtain water-soluble nanocellulose. Non-solvent (acetone) for nanocellulose was poured into the solution to accomplish its precipitation and performed two subsequent filtering by 0.45μm and 0.2μm filter papers. The nanocellulose was vacuum dried at 25°C for 24 hours and then again dissolved in the distilled water followed by freeze drying. The specimen, water-soluble ENC, was stored in the desiccator at 21±1°C and 65%±2% RH for characterization.

2.3 ENC Characterization

Esterification of nanocellulose was confirmed by Fourier-transform infrared (FT-IR) spectrophotometer (Bruker, Vertex 70, USA) attached with attenuated total reflectance at 4000-600cm^{-1} and 64 scans and 2cm^{-1} resolution. Particle size of ENC was evaluated in 0.5wt% aqueous solution by dynamic lighter scattering (DLS, Zetasizer nano ZS90, Malvern Instruments Ltd., UK). Three replications were performed and the average was obtained. DLS method could also measure surface charge of ENC. Surface morphology of ENC was investigated by scanning electron microscopy (SEM, COXEM, CX-100S, Korea) and its crystalline structure was studied by X-ray diffraction (XRD, D2 PHASER, Bruker, Germany) employing a Co-Kα (λ= 0.1524nm) source and operating range at 30 kV and 10 mA. The sample was scanned at a speed of 2 °/min with 0.02 increment for 2θ range of 75° to 2°. Crystallinity index was obtained from XRD spectra by using Segal method as follows [10]:

$$\text{Crystallinity Index (CrI)} = [(I_{cry} - I_{am})/I_{cry}] \times 100 \qquad (1)$$

where I_{cry}= peak intensity of crystalline area (2θ=30°) and I_{am} was peak intensity of amorphous area (2θ=26°).

Thermal characteristics of ENC were evaluated by thermogravimetric analyzer (TGA, Mettler, USA) at 25°C~700°C temperature range for 10°C/min rate under nitrogen atmosphere. Furthermore, the presence of COOH was examined by reverse-titration method of aqueous solution of ENC by using 1M of NaOH and 1M of HCl. Solubility of ENC was investigated as follows: 3g of the deionized water was placed in a 250mL round bottom flask installed in constant temperature oil bath at 60, 70 and 80ºC. The 0.01g of ENC was step-wisely added into the solution at one min. interval to confirm its solubility. The solubility was calculated as follows:

$$\text{Solubility(\%)} = (\text{weight of specimen dissolved}/3\text{g}) \times 100 \qquad (2)$$

2.4 Sorption of heavy metal on ENC

Sorption of heavy metal ions on ENC was investigated to examine its application as metal ion sorbent. Two mL of pH-controlled deionized water was prepared and appropriate amounts of ENC were added to the beaker to provide three concentrations (1, 3, and 5% w/w) of ENC solutions with 15 min of stirring. Three mL of 1000ppm Cu or Zn in forms of the standard solutions (Kanto Chemical Co., Inc, Korea) was added to the system and stirred for one hour. Thirty mL of acetone was then poured into the solution to precipitate ENC and passed through the filter paper with 0.02µm pore size. The sorption of metallic ion on ENC was evaluated by UV-Vis spectroscopy against the control solution. Beer-lambert law was used to measure concentration of the metallic ions as follows:

$$A = \varepsilon \times b \times c \qquad (3)$$

where A is the absorbance, ε is the molar absorptivity ($M^{-1}cm^{-1}$), b is the path length (1cm), and c is the analyte concentration. Sorption of Cu or Ze of the ENC specimens was compared against the standard solution. The following equation was used to calculate amounts of sorption per gram of ENC:

$$\text{Sorption of Cu or Zn ion per g of ENC (ppm/g)} = (Co-C)/m \qquad (4)$$

where Co is concentration of standard solution (ppm), C is solution concentration after sorption (ppm), and m = weight of ENC (g)

3. RESULTS AND DISCUSSION

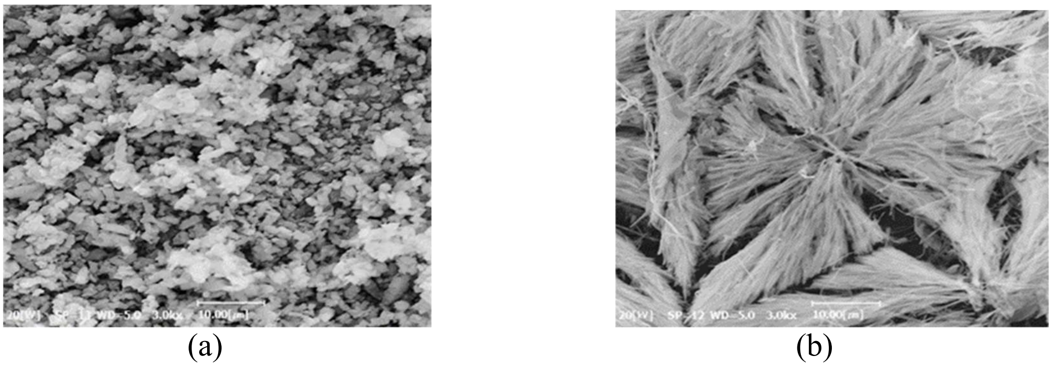
(a) (b)

Figure 1. Surface morphology of ENC (a) ENC prior to freeze drying (b) ENC after freeze drying

3.1 Size and shape of ENC

Particle size measurement of ENC indicated that their Z average sizes were in 1044~1202nm range, but peak intensity was around 484~550nm. Since Z average size in DLS was cumulative means, the results clearly indicated occurrence of ENC aggregation within solution. Aggregation was also substantiated by their size increase at consecutive measurements and it was due to the presence of hydrogen bonds between residual hydroxyl groups in ENC. SEM was also employed to study surface morphology of ENC. Figure 1 showed SEM micrographs of ENC particles before and after freeze drying. The specimen in Figure 1-(a) showed crystal-like shape of ENC prior to freeze drying. This micrograph suggested that their particle sizes were not uniform and tended to be slightly larger than nano level. On the other hand, Figure 1-(b) illustrated the ENC particles first dissolved in water followed by freeze drying process. These ENC particles were fiber-like shape at nano levels. The shape of these ENCs was quite similar to growth of nucleus in crystals. This was believed to be due to interaction of water and residual hydroxyl groups of ENC, resulting in smaller particles. Therefore, the shape of nanocellulose could be readily modified by applying different processes.

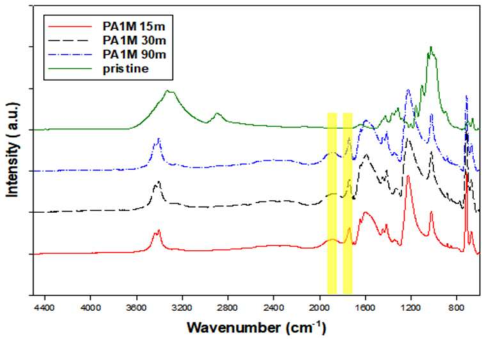

Figure 2. FTIR spectra of ENC specimens at various ultrasonic irradiation times

3.2 FTIR analyses

As shown in Figure 2, FTIR spectra of ENC treated at different ultrasonic irradiation times. Results indicated that ENC specimens clearly showed evidence of esterification by PA in absorption peaks at 1745cm^{-1} for ester C=O and 1646cm^{-1} for C=C in benzene ring. Furthermore, the peak at 1885cm^{-1} for asymmetric anhydride C=O was observed in ENC specimens. This was rather surprising since we did not expect to observe existence of anhydride absorption peak in ENC. This was due to existence of two different ester-forming reagents, PA and OA, suggesting participation of OA as a reactant as well as solvent in OAC. The potential reaction between PA and OA in OAC with cellulose could form various types of anhydrides in addition to conventional ester formed between PA or oxalic acid and cellulose hydroxyl group.

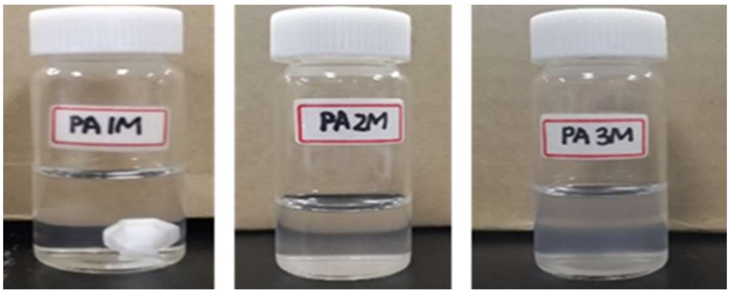

Figure 3. Aqueous ENC solutions prepared at different concentrations of PA at 80°C

3.3 Solubility of ENC prepared with PA

Figure 3 shows aqueous solubility of ENC specimens prepared with three levels of PA at 80℃. Results revealed that ENC solubility was increased with increase in solution temperature, but decreased with increase in PA concentration. Complete solubility of ENC reacted with 1mole of PA was clearly substantiated. Decrease in solubility at greater PA concentration was obviously due to the presence of hydrophobic benzene ring in PA molecule. This confirmed the cleavage of hydrogen bonds between cellulose chains during production of ENC, resulting in water solubility of nanocellulose. During the ENC production, OAC swelled cellulose molecules and irradiation by ultrasonic and microwave further enhanced esterification reaction, facilitating production of ENC with increased solubility.

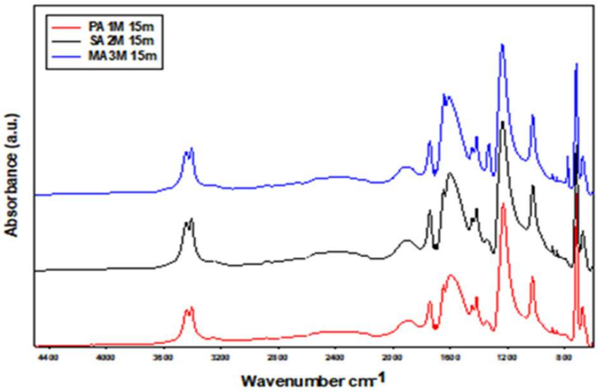

Figure 4. FTIR spectra of ENC prepared by various anhydrides

3.4 ENC prepared with other anhydrides

Since aromatic ring in PA tended to decrease solubility of ENC, we also examined other anhydrides such as maleic anhydride (MA) and succinic anhydride (SA) for ENC production. As shown in Figure 4, two carbonyl absorption peaks at 1800 and 1745cm^{-1} in FTIR spectra indicated the presence of mixture of ester and anhydrides even in ENC prepared by MA and SA just like PA. In addition, the ENC prepared by MA showed absorption peak at 1330cm^{-1} due to C-H bending vibration. Solubility analyses confirmed extremely high solubility in ENC prepared by MA due to the absence of benzene ring. However, solubility of ENC prepared by SA was even lower than that of ENC with PA. This tended to suggested that SA substitution did not initiate enough disruption of hydrogen bond within cellulose molecules, instead the treatment with SA added additional hydrophobic ethylene and ester groups consequently reduced hydrophilicity, resulting in lower solubility in water. Water solubility difference among three anhydrides was due to differences in pKa values as 1.9, 2.89, and 4.2 for MA, PA, and SA. Therefore, strong acidic MA not only increased the reaction rate, but also swelled cellulose molecules more, causing considerably greater solubility than that of ENC treated with PA and SA.

4. CONCLUSION

In this study, water soluble ENC was prepared by reaction cellulose with various anhydrides in OAC DES under ultrasonic and microwave irradiation. Results indicated that particle size of ENC was around 500nm. FTIR analysis substantiated various types of esters and anhydride groups caused by the presence of PA and oxalic acid within OAC DES. Thus, OA was participated not only as a solvent but also as a reagent in ester or anhydride formation with cellulose and/or PA. The trend was that at low ultrasonic irradiation time, crystallinity and thermal decomposition reached the minimum, started to increase with increase in irradiation times, and then decrease again. Esterification of nanocellulose affected on solubility in both positive and negative ways. The presence of strong negative charge was detected on surface of the PA-treated ENC by zeta potential measurement. Sorption of heavy metal ions such as Cu and Zn was investigated by this negatively charged ENC. Sorption of metal ions was influenced by three parameters such as pH and amounts of ENC in the solution, and concentration of PA that used in preparing ENC. As expected at alkaline pH such as pH 9, the PA-treated ENC sorbed the greatest amounts of Cu or Zn. Therefore, this water soluble, esterfied nanocellulose could be produced in very rapid and eco-friendly ways and this ENC could be used in various end-use applications in addition to sorbent application.

5. REFERENCES

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