Available online at www.scholarsresearchlibrary.com

Scholars Research Library

European Journal of Zoological Research, 2014, 3 (1):142-146
(http://scholarsresearchlibrary.com/archive.html)

ISSN: 2278–7356

Characterization of nanocrystalline cellulose obtained of cotton waste

Farid Amidi Fazli[1*], Mohammad R. Ehsani[1], Babak Ghanbarzadeh[2] and Gholam H. Asadi[1]

[1]Department of Food Science and Technology, Science and Research branch, Islamic Azad University, Tehran, Iran
[2]Department of Food Science and Technology of Tabriz University, Tabriz, Iran

ABSTRACT

Problems and disadvantages of using conventional plastics are more apparent in recent years and have attracted researchers' attention. Polymers from natural resources or bio polymers represent a suitable replacement to overcome to the disadvantages of plastics. But due to the some flaws of bio polymers, using suitable filler almost seems necessary. Nanocrystalline cellulose with low cost and availability can be applied as appropriate filler. In this study nanocrystalline cellulose was produced from cotton Linter and was characterized. The cotton Linter was hydrolyzed in sulfuric acid then neutralized by the two different concentrations of NaOH. The resulted suspension was treated by ultrasound waves. Process efficiency was determined as 90%. The final product was studied using x-ray diffraction technique. The obtained diagram of XRD experiment confirmed that the produced material was nanocrystalline cellulose. Also percentage of crystallinity was calculated as 84% in the obtained material as well as the size of crystals. It can be said that the applied method is a rapid and easy method for the production of nanocrystalline cellulose.

Keywords: Nanocrystalline cellulose, crystallinity, XRD, Cotton linter

INTRODUCTION

Cellulose is a constituent of cell wall in plants. This compound was used first in 1838. It can be found almost pure in cotton fibers. The strings are important in yarn, textile production and apparel manufacturing. Joining two molecules of β- glucose forms one molecule of Cellobiose. Every 5 molecules of cellobiose are arranged spatially in a cubic shape, form crystalline cellulose; crystalline cellulose may form initial cellulose fiber or micelles. Micro-fibrils of cellulose with about 25 nm in diameter are made of micelles. 20 micro-fibrils will create macro cellulose fibrils. Cellulose is made up of units which are called the initial string with a diameter of 35 Å; the diameter is often true but not guaranteed.

Nanotechnology is a way of creation of desired molecular structure with atomic precision. Since all of the products and the materials are made of the atoms in a specific order. Nanotechnology can be potentially used to produce all the products needed by human. Nano scale has existed for many years in human life although the present century, when the human is able to understand nanotechnology better and can control it more than past with the new approaches. Nanotechnology has been appeared as a revolution in making materials and systems.

Adding nanocellulose to caseinate sodium biofilm increases barrier properties of the biofilm against the water vapor although increasing amount of filler has reverse effect on barrier properties [1]. The use of cellulose nanoparticles in the matrix of starch film decreases the hydrophilic property of the film, especially when the glycerol is used as plasticizer [2]. To production of nanocellulose from wheat straw Kaushik et al. treated wheat straw by water steam then by acid, finally they applied high shear mechanical process to produce nanocellulose [3]. Production of nanocellulose from pea pods and applying it in pea starch biofilm have been investigated. In this way, pea pods were treated with sulfuric acid [4].

Non-biodegradable plastics in nature has created many environmental problems. Natural biofilms with high biodegradability obtained from renewable agricultural resources are ideal for being the replacement of non-biodegradable plastic products. A new method of improving the properties of biopolymers has been introduced by the arrival of nanotechnology in the field of polymer science. In this method, the nano scale fillers are added to matrix of biopolymers and the result would be biopolymer nanocomposites. The use of nanocrystalline cellulose in bio nanocomposites due to its appropriate functional properties has been interesting for many researchers in scientific as well as in industrial communities in recent years. Disadvantages of biopolymer films, especially the weaker mechanical properties and higher hydrophilicity in comparision to synthetic polymers, has limited widespread use of biopolymers.

The use of agricultural waste and the convertion of the waste into high value-added products is one of the proposed solutions to reduce production costs and increase production efficiency and productivity in the agricultural sector which makes optimal use of the available resources. Short cotton fibers or fluffs sticked to cotton which are called linter are not suitable for use in industry and are considered as waste. Cotton linter is a cellulose riched material, in case of converting linter to nanocrystalline cellulose, a value less agricultural waste will be converted to invalueble product.

Nanocrystalline cellulose or whiskers are rod-shaped particles with high crystallinity and with hundreds square meters per gram the specific interface. This nanostructure with mono crystalline, long and regular rod shaped as well as low cost is a suitable option for improving the mechanical properties of synthetic and natural polymers. Availability and renewability are important characteristics of the cellulose nanoparticles [5]. Due to non toxic and inert properties of nanocomposites made of nanocellulose, it is applied in pharmaceutical, food, paper, cosmetics, medical industries and prosthetic make.

X-ray Diffraction (XRD) is a method to study the crystalline structure of the materials which was discovered in 1912 by von. X-rays that are used for diffraction, have usually wavelength about 0.5 to 2.5 Å. X-ray diffraction method is a nondestructive analytical technique which provides information about the crystalline structure, symmetry and physical properties of the materials. By contacting X-rays, a form of electromagnetic radiation to the electron cloud around the atoms in the material, they are scattered in three dimensions. By studying of ray scattering patterns valuable information about the distribution of electrons around atoms will be achieved.

This study has been taken place to evaluate the possibility of nanocrystalline cellulose production from cotton linter; if the nanocrystalline cellulose could be obtained through the proposed process a material with high value added will be achieved. The benefit of using cellulose nanocrystal neutralization process by NaOH will accelerate the nanocrystalline cellulose production process; by applying concentrated NaOH solutions the amount of consumed NaOH solution will be decreased but concentrated NaOH solution should be applicable in practice.

MATERIALS AND METHODS

Cellulose micro fibrils are composed of two crystalline and amorphous regions, to extract nanocrystalline cellulose from cellulose amorphous regions of micro fibrils is removed by acid hydrolysis and crystalline regions will remain [6]. Nanocrystalline cellulose is generally prepared by a two-step procedure:
1) Initial hydrolysis to remove amorphous regions of cellulose;
2) Crashing of crystalline structure to produce nanocrystalline cellulose.

Among all methods of preparation, acid hydrolysis which is followed by crashing is a way to production of nanocrystalline cellulose. The amorphous regions of cellulose molecule will be removed during hydrolysis [7, 8].

In this study nanocrystalline cellulose was extracted from cotton linter. Cotton linter was cut into small pieces about 2 cm lengths by scissors then washed with distilled water. Then the cut linter was gone under hydrolysis treatment by sulfuric acid (65% w/w). The weight ratio of cotton linter to sulfuric acid was 1:20. Extraction process is based on the fact that crystalline regions remain unsolved in acid solution; in other words, disordered structure of cellulose in the amorphous regions are sensitive to acid hydrolysis [9]. Hydrolysis took place at 55 ˚C and under continuous stirring for 2.5 h.

In order to neutralize the acidic suspension of NCC, the NaOH solution was used at the concentration of 10% and 40% (w/v). The titration procedure continued until the pH of suspension was reached to 5.5-6. After neutralization washing step with distilled water was performed for 1 h at 15 min intervals. Finally the obtained suspension was treated with ultrasound waves. A 40 kv power ultrasound equipment was performed and treatment applied for 15 min. In order to ensure the production of nanocrystalline cellulose samples were analyzed by X-ray diffraction experiment.

XRD is based on the wave properties of the X-ray. Nuclei of atoms in crystal lattice spacing about a few angstroms from each other. X-ray reflection from the parallel sheets of the crystalline structure creates constructive or destructive interference. In the case of constructive interference, the distance between the crystal sheets as well as dimensions and type of the unit crystalline cell would be estimated. Bruker Advance D 5000 model X-ray generator manufactured by Siemens, Germany was applied to perform X-ray diffraction analysis. To perform the test, X-ray generator power was set to 40 kv and 30 mA. Samples were prepared and subjected to X-ray with wavelength of 0.1539 nm. Emitted radiations in the range of 2θ = 1-40 ˚ gathered from the sample at room temperature. Test Speed set at 1˚/min and step value was 0.05˚. Intension of the emitted rays plotted verse the radiation degrees.

To determine the yield of process, the amount of useful product obtained or NCC divided by the amount of cotton linter as raw material consumed to produce NCC from cellulose, the result was multiplied by 100. The following equation was used to calculate the efficiency of the process.

$$efficiancy = \frac{Dry\ NCC}{Initial\ cottton\ linter} \times 100 \qquad (1)$$

Since the used method produces NCC suspension, to determine the amount of NCC dry matter of obtained suspensions was measured according to AOAC standard method [10].

$$DM = \left(\frac{final\ weight}{Initial\ weight}\right) \times 100 \qquad (2)$$

For this, certain amount of suspension homogenized then weighted and dried at 100 °C in an oven until constant weight was reached. The difference between initial and final weight represents the water content of the sample or on the other hand it represents the dry matter content of the sample.

To determine the crystallinity of nanocrystalline cellulose Segal method was applied [11]. According to this method the amount of cellulose crystallinity equals to:

$$CI = \frac{I_{200} - I_{AM}}{I_{200}} \times 100 \qquad (3)$$

CI is the NCC crystallinity Index
I_{200} is the height of the 200 peak (2θ= 22°)
I_{AM} is the minimum height between the 200 and 110 peaks (2θ= 18°).

The size of crystals can be determined thorough the data obtained from x-ray diagram. Scherrer equation was used to determine the crystal size.

$$D = \frac{k\lambda}{\beta cos\theta} \qquad (4)$$

D is the NCC size,
K is Scherrer constant value
λ is the x-ray wave length (1.539 Å)
β is the peak full width half maximum
θ is the degree of observed peak.

RESULTS AND DISCUSSION

After the process completed stable aqueous suspension of nanocrystalline cellulose with 2.77% dry matter was obtained. Process yield based on the amount of consumed initial material and produced NCC was 90%.

X-Ray Diffraction results of the experiment are shown in Figures 1 and 2. As it seems in Figure 1 no peak was observed, this indicates that no crystalline regions existed in the sample and only amorphous regions are found.

That sample had been neutralized by 40% (w/v) concentration of NaOH solution. Therefore, this method is not suitable for production of nanocrystalline cellulose. In Figure 2, the neutralization was performed by 10% (w/v) concentration of NaOH solution. As can be seen in Figure 2 peaks are appeared.

Observed Peaks in XRD diagram indicates the crystalline regions in the examined sample. The peaks appeared at the angles of 14.7, 16.5 and 22.7˚. These angles are specified for the nanocrystalline cellulose structure under mentioned analysis condition.

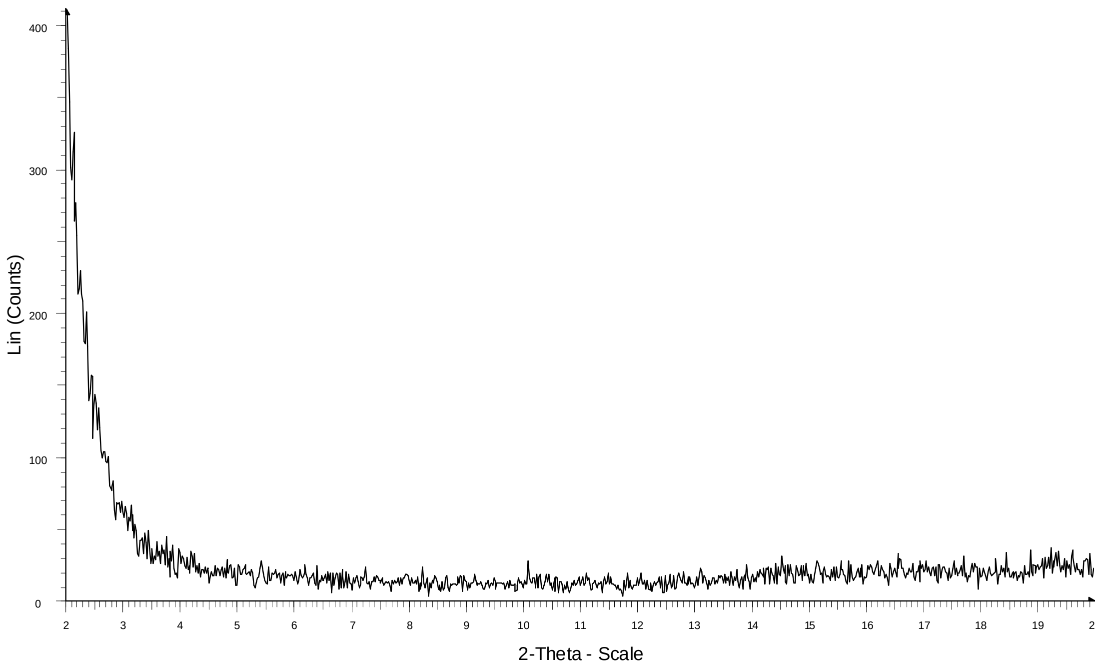

Fig.1. X-Ray diagram for obtained material which was neutralized by 40% NaOH

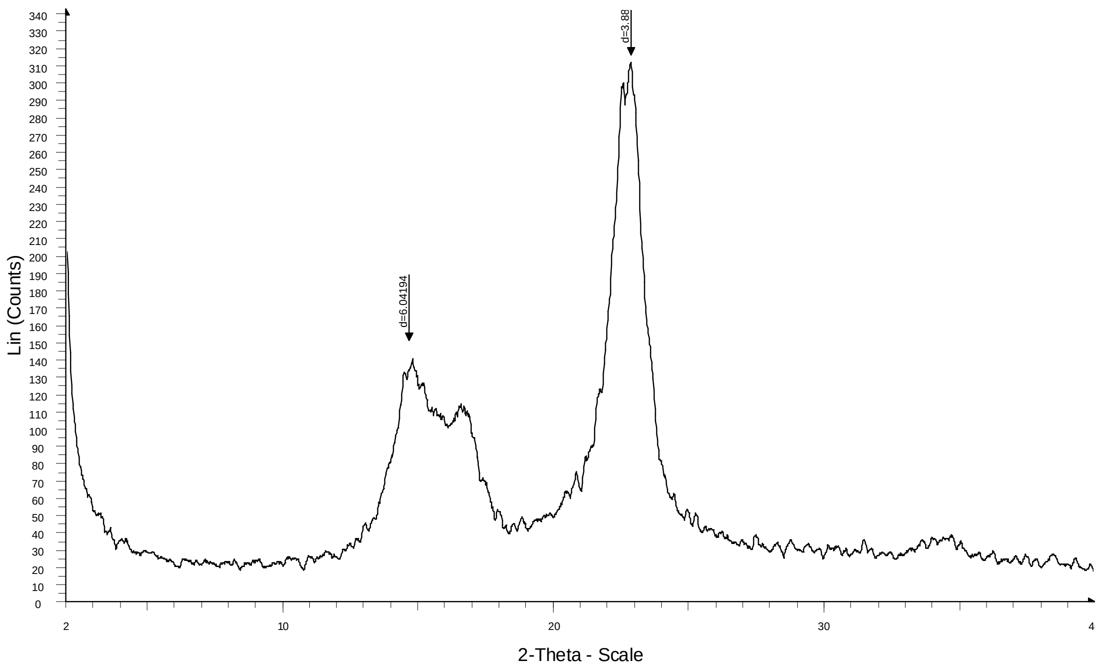

Fig.2. X-Ray diagram for obtained nanocrystalline cellulose

According to Segal equation the crystallinity of NCC is equal to the ratio of the amount of crystalline region to total amount of material containing both crystalline and amorphous regions. The observed peak in XRD diagram at 2θ= 22° represents both crystalline and amorphous regions while the peak observed at 2θ= 18° represents amorphous region. Using the Segal equation crystallinity of the obtained NCC was calculated as 84.59%.

$$CI = \frac{305 - 47}{305} \times 100 = 84.59\%$$

This value is higher than the Crystallinity index which is reported by Thygesen *et al.* [12] for Corn stover, Norway spruce, Hemp fibres and Avicel cellulose as 47, 47, 77 and 62% respectively and is in agreement with the crystallinity of Filter paper cellulose (83%). Calculations showed that the size of the crystals in obtained NCC during the production process according to the Scherrer method was 6.15 nm.

According to the results obtained in this study it is agreed that the neutralization step should be performed by NaOH solution with 10% (w/v) concentration. It should be mentioned that all procedures were the same for both samples except the concentration of NaOH solution in the neutralization process. It is concluded that applied method have been leaded to the production of nanocrystalline cellulose with crystalline structure.

CONCLUSION

Cotton linter, a cheap and available agricultural material, can be used to produce nanocrystalline cellulose. In the applied method acid hydrolysis followed by ultrasound treatment was used to produce nanocrystalline cellulose. The process leads to the production of nanocrystalline cellulose. It should be noted that the 40% concentration of NaOH solution is not an appropriate material to neutralization step then for neutralization of acidic solution of nanocrystalline cellulose 10% concentration of NaOH is recommended. In future researches the differences in properties of the nanocrystalline cellulose also can be studied by changing process conditions. In the case of transforming the accumulated cotton waste in oil extraction plants or other cotton related industries to nanocrystalline cellulose, the efficiency of agricultural activities will be increased in this way. One of these methods is to collect linter or cotton waste and sending them to the nanocrystalline cellulose manufacturing plants. By creation of such plants in major cotton production areas, the cost of cotton production will be reduced on the other hand one of initial materials needed for production of bio nanocomposites will be provided.

REFERENCES

[1] M. Pereda, G. Amica, I. Rácz, N.E. Marcovich, *J. Food. Eng.*, **2011**, 103, 1, 76-83.
[2] E.M. Teixeira, D. Pasquini, A.A.S. Curvelo, E. Corradini, M.N. Belgacem, A. Dufresne, *Carbohyd. Polym.*, **2009**, 78, 3, 422-431.
[3] Kaushik, M. Singh, G. Verma, *Carbohyd. Polym.*, **2010**, 82, 2, 337-345.
[4] G. Chen, A. Dufresne, J. Huang, P.R. Chang, *Macromol. Mate. Eng.*, **2009**, 294, 59-67.
[5] Siró, D. Plackett, *Cellulose*, 2010, 17(3), 459-494.
[6] W.E. Gacitua, A.A. Ballerini, J. Zhang, *Cienciay techn.*, **2005**, 73, 159-178.
[7] D. Silva, L. dalmedia, *O Papel*, **2009**, 70, 34-52.
[8] A.P. Mathew, W. Thielemans, A. Dufresne, *J. Appl. Polym. Sci.*, **2008**, 109, 4065-4074.
[9] D, Bondeson, A. Mathew, K. Oksman, *Cellulose*, **2006**, 13, 171-180.
[10] AOAC, Association of Official Analytical Chemists, 17th Ed. of A.O.A.C. International. Published by A.O.A.C. International. Maryland, USA, **2000**.
[11] L. Segal, J.J. Creely, A.E. Martin, C.M. Conrad, *Text. Res. J.*, **1959**, 29, 786 –794.
[12] Thygesen, J. Oddershede, H. Lilholt, *Cellulose*, **2005**, 12, 563–576.