CRYSTALLINE CELLULOSE AS BIONANOCOMPOSITE FIBER FOR ANTIMICROBIAL PACKAGING APPLICATION

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ABSTRACT

Over the decades in the medicinal field, biodegradable polymers offer tremendous potential either as a drug delivery system alone or in conjunction to functioning as a medical device. Significantly, cellulose reinforced polymer matrix containing smaller size fibers exhibits enhanced physical, mechanical and biological properties as compared to the pristine polymer matrix containing larger size fibers. In the present work, a study on the feasibility of isolating cellulose from the crop residue of rice husk waste was carried out. The surface morphological investigation and the size of the extracted cellulose crystals were studied. Fourier transform infrared (FT-IR) spectra of the cellulose showed the efficient removal of non-cellulosic constituents. X-ray diffraction (XRD) analysis revealed the three main diffraction peaks at 2θ values of $17.8^{o,}$ $22.7^{o\,,}$ and 34.4^{o} relative to the cellulose crystalline structure and the crystallinity index of the cellulose was found to be 70 ±3 %. Thermo gravimetric analysis (TGA) showed that the crystalline cellulose decomposed at $333^{o}C$ and further no additional peaks were observed indicating the purity of the extrated cellulose. These results showed that the extracted cellulose possessed significant thermal stability and higher yield which could be used for advanced biocomposite nanofiber which could be utilised in the packaging applications.

Keywords: Cellulose, biopolymer, biocomposite, crystallinity, nanofibers

INTRODUCTION

In the recent decades, cellulose and cellulose-based bionanocomposites are reported to offer many advantages including world wide availability, low cost, easy manipulability, and good processability [1,2]. More tones of agricultural residues are generated every year, with only a small percentage residue being used in applications such as feedstock and energy productions. The use of agricultural residues in biocomposites production is a prospective commercial application that would be the significant potential of these underutilized renewable materials and provide a non-food based market for the agricultural industry. Although there are some useful studies on agricultural fibers in biocomposites [3-7], the fibers produced in these studies have not yet attained sufficient improvement in their physical, mechanical and thermal properties to be used in applications. The production of biodegradable composites uses natural cellulose fibers, which have been the subject of extensive research. The reinforcement of nano-cellulose in biocomposites fibers has fascinated significant attention due to their huge naturally abundance, large surface area, good mechanical strength, etc [5].

Plant cell walls consist of cellulose fibrillar component. Cellulose has a linear homopolymer chain of β-(1→4)-linked glucopyranose units. Cellulose chains are arranged in an ordered manner to form elementary microfibrils by hydrogen bonds [8]. Cellulose I has two phases, I_α and I_β. Cellulose I_α, occurs only in some green algae plants along with I_β. However, cellulose I_β exists in an almost pure state over a world wide range of plants. In addition, both the forms of cellulose are reported to frequently coexist in plants with amorphous cellulose [9-10].

Comparing the production of cellulose nanoparticles from microcrystalline cellulose, cotton, flax, and hemp fibers, the nanoparticles from agricultural residues might be more economical. Rice husk is a low cost and renewable resource suitable for producing bio composites. In addition, Rice husk fibers have a thick layer on its surface composed of non-cellulosic materials such as lignin and hemicelluloses. The presence of hydrophobic wax layer on the surface of husk resists its degradation from moisture. Hence, it is used as a better reinforcing agent in the preparation of bio-composites. Many researchers [11-14] have used different methods of processing from different source of cellulose to obtain nano-cellulose in the recent years. Among the various methods, acid hydrolysis alone or in combination is reported to be well known and a widely used method [14-17].

In this work, an efficient synthesis has been made to extract the cellulose from the crop residue – rice husk to use it as filler in the production of biocomposite nanofibers. We have utilised a chemical treatment and low cost, higher yield which resulted in increased crystallinity and thermal stability of ellulose with an appreciable molecular weight. This synthesis procedure involves the use of, common non-hazardous chemicals at low concentration, simple equipment, easy to work and eco-friendly methods. Moreover, this method provides minimum energy consumption and is more economical and gives significant yield and good quality of the product. The prepared cellulose was systematically characterised.

1 MATERIALS AND EXPERIMENTAL DETAILS

1.1 MATERIALS

Rice husk was obtained from the local agricultural land in Tamil Nadu and used in the present work. Ethanol, Sodium hydroxide (NaOH), Sulphuric acid (H_2SO_4), Hydrogen peroxide(H_2O_2), and Nitric acid (HNO_3) were purchased from Fischer Scientific Company. All the reagents of analytical grade were used.

1.2 EXTRACTION PROCEDURE

The rice husk fibers were subjected to pre-treatment to remove impurities and waxy materials. Next, it was treated by adding 4% H_2O_2 solution at 45°C followed by hydrolysis with 70% HNO_3 at 30°C under continuous agitation. Finally, the product was washed with distilled water and ultra-sonicated under 100W at 60°C for 30min in order to individualize the fibre bundles. Then the cellulose was vacuum filtered and dried at 60°C for 24 h in oven [18].

1.3 MEASUREMENTS AND CHARACTERISATIONS

FT IR Spectroscopy (Perkins-Elmer Spectrum RX100) in the range of 400 cm^{-1} to 4000cm^{-1} was used to characterise the functional groups of the extracted cellulose. The morphological features of the product obtained was studied using SEM (FEI Quanta FEG 200 HRSEM) and the diameters of the extracted cellulose fibers were measured using the Adobe Photoshop CS3 Extended Software PS version 10.0 model. The particle size distribution of the extracted cellulose was studied using a Malvern Zeta Sizer Nano-S Version 7.03. The molecular weight and polydispersity index of prepared cellulose was analyzed by Gel

Permeation Chromatography (GPC), using Tetrahydrofuran (THF) containing 0.2 wt% LiCl as an eluent using Polystyrene standards. It was carried out at 80°C at a flow rate of 0.6 ml/min using a refractive index detector. XRD patterns of the extracted cellulose was analysed using a X'pert Pro PANalytical Instrument using Cu Kα radiation (λ=1.5418 A^o) in the 2θ scale from 5^o-60^o. In addition, the percentage of crystallinity index of the extracted cellulose (i.e X_c %) was calculated from the diffraction intensity data using the following equation [17].

$$\% \text{ Crystallinity index} = \frac{I_{002} - I_{amorph}}{I_{002}} \times 100 \qquad (1)$$

The thermal degradation characteristics of the extracted cellulose was examined using thermogravimetric analysis (TGA/DTA Model SDT 2600) at a heating rate of 10^oC/min from 35^oC to 800^oC with continuous nitrogen flow of $20cm^3$/min.

2 RESULTS AND DISCUSSION

2.1 EXTRACTED CELLULOSE

In particular, the raw material rice husk was subjected to a delignification process in order to simplify the extraction method. Then, the crushed raw fibers were added with alkali to remove the waxy materials from the cell wall. Next, the fibers were treated with sulphuric acid led to more removal of non-cellulosic substances. Further, the fibers were treated with HNO_3 increased the crystallinity and molecular weight of cellulose fibers producing in a better yield and good quality of the extracted cellulose [15].

2.2 FT-IR MEASUREMENTS

FT-IR analysis can investigate the changes occurring in the chemical composition of the rich husk fibers before and after the chemical treatment. The FT-IR spectra of the untreated rice husk and cellulose are shown in Figure 1. It can be observed that the hydrophilic nature of both rice husk and cellulose are reflected by the broad absorption peak at the 3700-3200 cm^{-1} region corresponding to the presence of -OH group [13]. The peak in the 1635–1655 cm^{-1} region is attributed to O-H stretching due to absorbed water. The peaks at 2900–2920 cm^{-1} are assigned to the aliphatic saturated C–H stretching vibration in cellulose. The intensity of the peaks at 1430, 1330, 1264, 1161, 1062 and 896 cm^{-1} have increased in cellulose indicating the typical structure of cellulose (β-(1→4)-glycosidic linkage) [19-20]. In addition, a slight absorption band at 896 cm^{-1} is designated as an amorphous band and a strong absorption band at 1429 cm^{-1} assigned to the symmetric CH_2 bending vibration is known as the crystallinity band, which reveals the high degree of crystallinity of the extracted product cellulose.

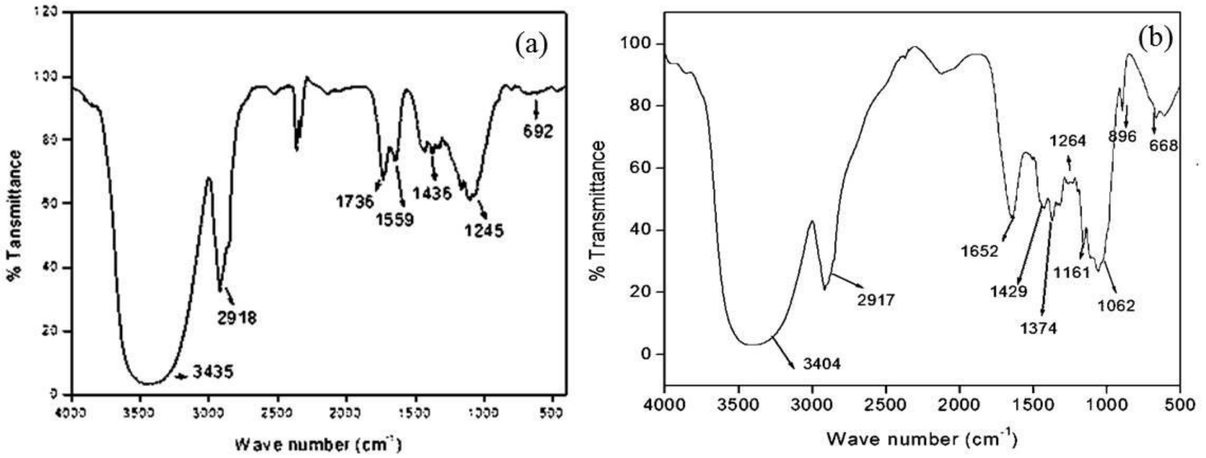

Figure 1. FT-IR spectra of (a) Untreated risk husk fibers (b) Cellulose

2.3 MORPHOLOGY ANALYSIS

The SEM micrographs of untreated raw fibers and cellulose are shown in figure 2(a) – (b). The SEM image of the extracted cellulose product showed the cellulose fibrils as aggregates on the surface. Typically, the average diameter of the cellulose fibrils were found to be about 800-900 nm, which are lower than the average size (100-250 μm) of the untreated raw fibers. The reduction in the fiber diameters are due to the efficient removal of the non-cellulosic substances such as lignin and hemicellulose. These results are also supported by the FT-IR analysis.

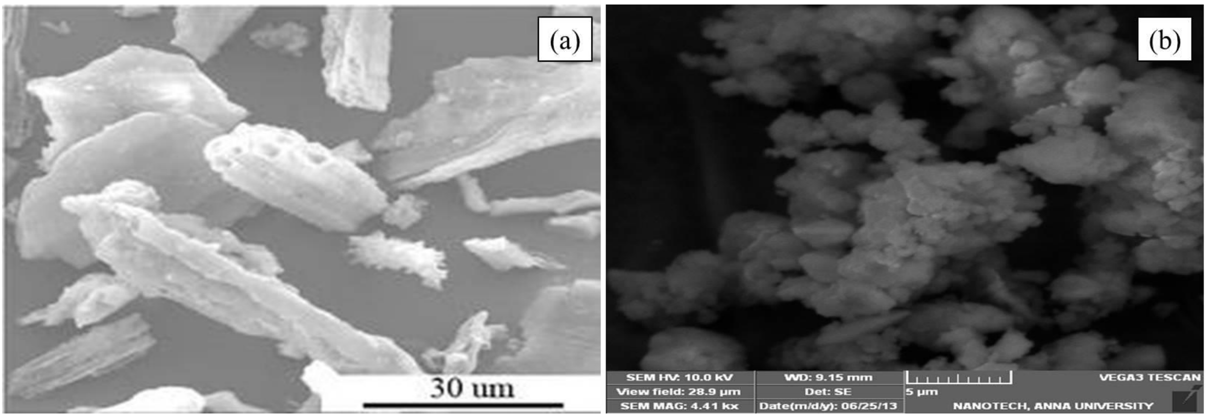

Figure 2. Surface Morphological features of (a) Untreated raw fibers (b) Cellulose

2.4 PARTICLE SIZE DISTRIBUTION

The average particle diameter of the extracted cellulose after the chemical treatment was measured. The average size distribution of the extracted cellulose is shown in figure 3. The chemical treatment of rice husk fibers yielded mono-disperse cellulose with a typical dispersion of nanosized fibrils. Most of the cellulose particles were found in the diameter range of 700-955 nm. These results show that the diameter of the cellulose fibrils reduced to nanoscale range after the chemical treatment and ultra-sonication. The chemical treatment used for synthesising cellulose from rice husk provided a viable and simple method of producing cellulose with an Z-average diameter of 1.0 µm.

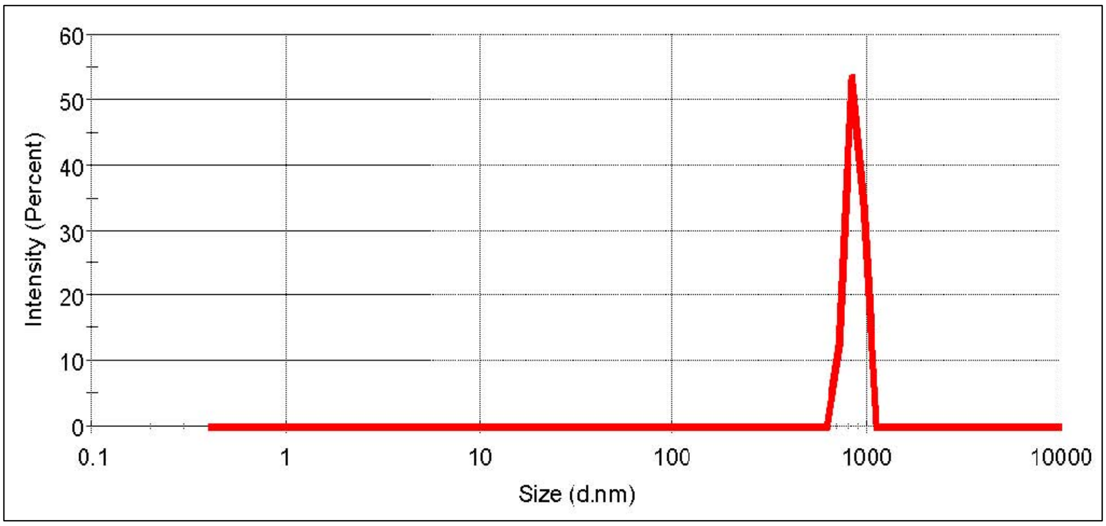

Figure 3. Particle Size distribution of extracted cellulose

2.5 MOLECULAR MASS DISTRIBUTION

The molecular mass distributions of the extracted cellulose are shown in Figure 4. Table 1 shows the Number-average (M_n) , Weight-average (M_w) and Z-average (Mz) molecular weights, and Polydispersity index (M_w/M_n) of the extracted cellulose calculated by the GPC chromatogram.

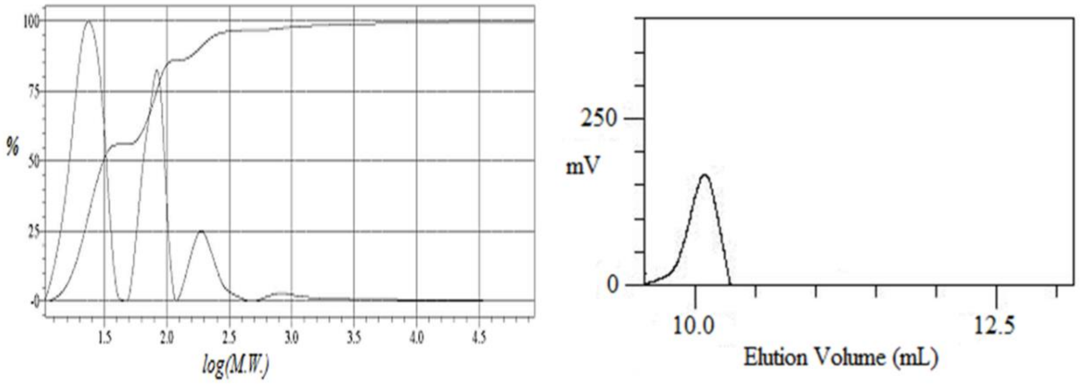

Figure 4. GPC molecular mass distributions of extracted cellulose

Table 1. Molecular mass distributions of extracted cellulose from rice husk

Molecular weight	g mol^{-1}
Number-average (M_n)	16,586
Weight-average (M_w)	22,272
Z-average (M_z)	30,758
Polydispersity index ($M_{w/}M_n$)	1.34283

2.6 X-RAY DIFFRACTION ANALYSIS

The X-ray diffraction pattern of the extracted cellulose is reported in Figure 5. As shown in the Figure 5, the presence of peaks at 2θ values of 17.8°, 22.7°, and 34.4° are characteristic of $(10\bar{1})$, (002), and (040) planes of cellulose respectively indicating the crystalline structure of cellulose-I [21]. The percentage of crystallinity index of extracted cellulose is given in Table 2. These results show that the higher crystallinity index of extracted cellulose are attributed to the efficient removal of lignin, hemicelluloses and other non-cellulosic materials and effective reorganization of amorphous and para crystalline cellulose region. These results also further confirmed that the crystalline regions of cellulose were stable while the acid hydrolysis took place preferentially in the amorphous region which caused the dissolution in the amorphous state thereby resulting in the increase of crystallinity of cellulose as reported by many researchers for the case of extraction of cellulose from banana fiber, viscose staple, bagasse, ramie, and cotton respectively [22].

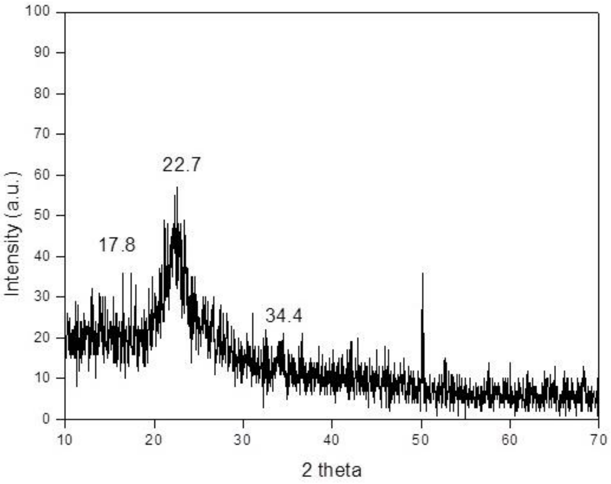

Figure 5. XRD pattern of extracted cellulose

Table 2. The crystallinity index of cellulose

Sample	I(amorphous)	I(002)	% Crystallinity index
Cellulose	46	155	70.3

2.7 THERMOGRAVIMETRIC ANALYSIS

The thermogravimetric analysis is an important tool to measure the applicability of the extracted cellulose to be used to prepare biocomposites for various applications. TGA thermograms of untreated rice husk and extracted cellulose are shown in Figure 6. It can be observed from the thermogram, that there was a first weight loss up to 120^{o}C which indicates removal of moisture and solvents. The cellulose started to decompose at 230^{o}C, whereas the untreated fibers started to decompose at a higher temperature of 250^{o}C. It could be seen that the prepared cellulose started decomposing at lower temperature than the untreated rice husk which are attributed to the presence of lignin in the rice husk. The decomposition rate of lignin occurs with continuous mass loss over the range of 200-700^{o}C. Further, the maximum weight loss in the case of cellulose occurred at 333.2^{o}C and no additional peaks were obtained indicating the purity of the extracted cellulose. After heating to 600^{o}C, relatively small amount of solid residue in the cellulose was observed which may be due to the carbonaceous materials in rice husk in N_2 atmosphere. From these results, the lesser amount of solid residue and better thermal decomposition of cellulose are related to more efficient removal of lignin and hemicellulose from rice husk fibers and higher crystallinity of the extracted cellulose [23]. The thermal stability of the extracted cellulose shows its applicability for bio composite nanofiber applications.

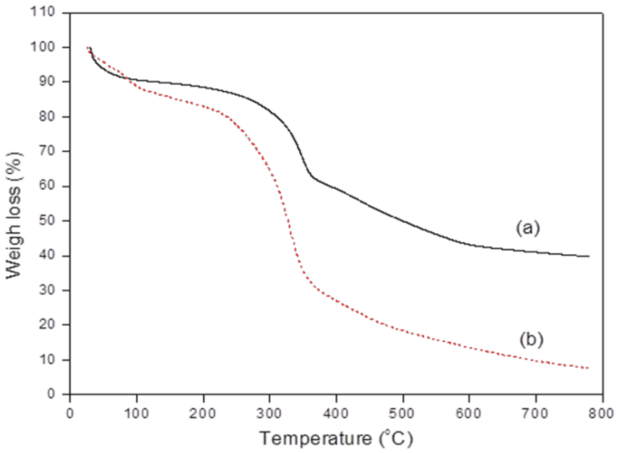

Figure 6. TGA thermograms of (a) Untreated rice husk (b) Extracted cellulose

CONCLUSION

In the present work, cellulose was extracted successfully from the agricultural residue rice husk fibers. The morphology and size distributions of the cellulose were characterized. The FT-IR measurement showed that the efficient removal of non-cellulosic substances such as lignin and hemicelluloses from the rice husk fibers by the successive chemical treatment. Furthermore, the crystallinity and thermal characterisation showed that the extracted cellulose exhibited enhanced physical and chemical properties stimulating the use of cellulose fibers as a reinforcing agent for the production of biodegradable nanocomposite fibers for the antimicrobial packaging applications.

REFERENCES

1. A. Alemdar, M. Sain, Bioresour. Technol., 99, 1664-1671 (2008).
2. M. A. S. Azizi Samir, F. Alloin, A. Dufresne, Biomacromolecules, 6(2), 612–626 (2005).
3. N.M. White, M.P. Ansell, J. Mater. Sci., 18, 1549-1556 (1983).
4. M. Ramamoorthy, S. Rajiv, Carbohydr. Polym., 133, 328-336 (2015).
5. P.R. Honsby, E. Hinrichsen, K. Tarverdi, J. Mater. Sci., 32, 443-449 (1997a).
6. S. Jonasson, A. Bunder, T. Niittyla, et al., Cellulose 27, 185–203 (2020).
7. Zi-Jing He, Kai Chen, Zhi-Hua Liu, et al., Journal of Cleaner Production, 414, 137708 (2023).
8. A.W. Zykwinska, M.C.J. Ralet, C.D. Garnier, J.F.J. Thibault, Plant Physiol., 139, 397-407 (2005).

9. R.H. Atalla, D.L. VanderHart, Science, 223, 283-285 (1984).

10. A. Sturcova, I. His, D.C. Apperley, J. Sugiyama, et al., Biomacromolecules, 5, 1333-1339 (2004).

11. D. Ye, Progress in Chemistry, 19(10), 1568–1575 (2007).

12. N.F. Adriana, M.P. Denis, D. Dan, U.P.B. Sci. Bull., Series B, 73(2), 133-152 (2011).

13. K. Anupama, S. Mandeep, Carbohydrate Research, 346, 76-85 (2011).

14. A. Ayse, S. Mohini, Biores. Tech., 99, 1664-1671 (2008).

15. M.F. Rosa, E.S. Medeiros, J.A. Malmonge, et al., Carbohydrate Polymers, 81(1),83-92 (2012).

16. S.Y. Lee, D.J. Mohan, I.A. Kang, et al., Fibers and Polymers, 10(1),77-82 (2009).

17. M. El-Sakhawy, M.L. Hassan, Carbohydrate Polymers, 67(1), 1-10 (2007).

18. R.C. Sun, X.F. Sun, Carbohydrate Polymers, 49, 415-423 (2002).

19. G. Socrates, New York, John Wiley & Sons., p. 366 (2004).

20. J.M. Fang, R.C. Sun, J. Tomkinson, Cellulose, 7, 87–107 (2000).

21. D. Ciolacu, F. Ciolacu, V.I. Popa, Cellulose Chem. Tech., 45(1-2), 13-21 (2011).

22. B.M. Cherian, L.A. Porthan, T. Nguyen-chung, et al., Agri.Food. Chem., 56, 5617-5627 (2008).

23. S. Panthapulakkal, A. Zereshkian, M. Sain, Bioresour. Tech., 97, 265-272 (2006).