

Analysis on Physiochemical Properties of Cellulose Fiber from Rice Straw Waste

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Abstract. Green biobased polymeric membranes are being increasingly studied for different applications. In this study, freeze dried cellulose fiber with 35% yield was isolated from rice straw. The cellulose fiber was obtained through bleaching and delignification of the rice straw waste using soxhlet instrument and facile method of alkali treatment, respectively. The cellulose fiber was analysed through X-ray powder diffraction (XRD), fourier-transform infrared spectroscopy (FTIR), zeta potential analyzer and scanning electron microscope (SEM). Compared to the straw, all physicochemical properties of treated cellulose fiber increased with zeta potential up to -33.61 mV. FTIR revealed that the treatments on the straw was successful to obtain cellulose fiber with high purity. In addition, the morphological study illustrated cellulose fiber with organized structure.

1. Introduction

Researchers have been concerned using agro-waste for producing eco-friendly materials and applications to reduce environmental issues including toxicity and reduction in landfill space [1, 2]. For example, burning rice straw (RS) as a second highest agro-waste leads to the health risks of air pollution, and effects on organic matter with huge nutrient losses [3]. Similar to other plant-based resources, RS contains high ratio of cellulose fiber [4]. With high demand of using nanotechnology, cellulose fiber ($C_6H_{10}O_5$), one of the unique organic polymers on earth is becoming more popular for different applications. Cellulose fiber contains a high number of glucoses which are linked by β -1,4-glycosidic in linear chain formats. It possesses remarkable structural advantages including high porosity, pore interconnectivity, large surface-to-volume ratio, low density, and hydrophilicity and good physicochemical characteristics [5, 6]. Among various methods of cellulose fiber isolation, alkaline treatment is a facile and economical method to remove lignin, hemicelluloses and pectins from plant-based materials. This treatment caused removing amorphous region while crystal region is protected to obtain cellulose fiber with high crystallinity and purity. In this work, freeze-dried cellulose fiber was extracted from RS by using soxhlet instrument, sodium chlorite, acetic acid and alkali treatment. RS and cellulose fiber were analyzed by XRD, FTIR, zeta potential analyzer and SEM.

2. Experimental

In this work, RS was obtained from Malaysian Agricultural Research and Development Institute (MARDI). All chemicals were analytical grade as purchased from Sigma-Aldrich (St Louis, MO, USA) without further purification. For bleaching process and cellulose fiber isolation from RS, potassium hydroxide (KOH, 85%, EM Science), sodium chlorite ($NaClO_2$, 80%, Fluka) and acetic acid glacial



(CH₃COOH) were used. The aqueous solutions were freshly prepared using double deionized water (DD water) (18.2 MΩ·cm) from a Millipore Direct-Q 5 Ultrapure Water System. All glassware used in this work were cleaned with HNO₃/HCl (3:1, v/v) and DD water followed by the drying process.

2.1. Cellulose fiber Isolation from rice straw

Similar to different biofiber sources, cellulose fiber isolation process from RS was carried out through removing and bleaching the unwanted components and lignin. RS was washed several times with the tap water to remove dirt and dusts, followed seven days air drying in a dark room. Then the dried RS was ground and milled with a 55 micro-mesh screen. To obtain dewaxed rice straw (DRS), a 30 g RS powder was initially dewaxed to dissolve oil, wax and pigment by a 2:1, v/v toluene/ethanol (450 mL) aqueous solution in a soxhlet instrument for 12 h at 70°C using an oil bath. The pasty dark brown color sample was washed with distilled water three times and extra liquid was decanted using a lab suction filtration unit (equipped with a whatman filter paper), followed drying process in a 60°C oven for 24 h. To remove lignin, DRS powder was mixed with a 1000 mL aqueous solution of sodium chlorite (1.4%) as adding drops of acetic acid tuned the pH at 3.0-4.0 and temperature at 70°C with gentle magnetic stirring for 5 h, followed washing and decanting of extra liquid several times which resulted obtaining light yellowish solid sample.

After that, the sample was leached through applying a 600 mL aqueous solution of KOH (5%) at the ambient temperature for 12 hours, followed by pouring 10 fold ice cubes immediately into the solution. The aqueous sample (~300 mL) was centrifuged with speed of 12000 rpm and dried by freeze-dryer apparatus (FreeZone 1.0 L Benchtop Freeze Dry System) to finally obtain the white pulpy cellulose fiber sample which was named CF.

2.2. Characterization

X-ray diffraction (XRD) analysis was used to evaluate the crystalline phases of samples at scintag XDS 2000 powder diffractometer. The samples were compressed between two smooth glass films. XRD was performed under ambient condition upon dispersion 2 angles of 5°- 40° with step size of 0.02° and scanning rate of 2 s/step as utilized a Ni-filtered Cu K radiation (= 1.5406 Å), an operating voltage of 45 kV, and a filament current of 40 mA. Model XPert Pro Panalytical Diffractometer was also used to measure the purity and crystallinity values of the sample [7]. Chemical and super-molecular structural analysis during preparation of CF as a modified natural fiber from RS can be determined by FTIR spectroscopy. FTIR (ThermoNicolet, USA) was employed to measure FTIR Spectra under ambient condition. First the sample was crushed with KBr with the ratio of 1:100, w/w and compressing into a transparent pellets. The spectra was evaluated at the transmittance mode in the range between 4000 to 400 cm⁻¹ with a 4 cm⁻¹ resolution and an accumulation of 128 scans. Scanning electron microscope (SEM) (XL 30- SFEG, FEI/Philips, USA) was used to measure surface morphology and microstructure of CF sample. A 5-kV accelerating voltage and an 8-mm working distance were applied for observation of the sample. The samples were mounted on the aluminum base with conductive carbon tape and deposited with gold at vacuum (20 mA for 2 min (Bio-Rad SEM coating system)).

3. Results and discussion

3.1. X-ray powder diffraction (XRD)

XRD evaluation on RS, DRS and CF are indicated in figure 1. These samples displayed a peak approximately at $2\theta = 16.5^\circ$, 22.5° and 34.6° as are in agreement with normal cellulose-I structure [8]. The cellulose crystals displayed feature allocations of 110, 200, and 004 planes, respectively [9]. Two peaks at 2θ of 16.11° and 22.23° could respectively represent the amorphous and crystal regions of the samples. As was expected the crystallinity and the intensity of peaks increased with applying treatments on the RS. The main elements in the amorphous region of RS are hemicellulose and lignin which were peeled out and be hydrolyzed during the alkaline treatment. Therefore, amorphous region was gradually

removed after each treatment while the crystal region was protected[10]. This result shows that the treatment enhanced surface alignment, crystal interfaces and hydrogen bonds of obtained materials.

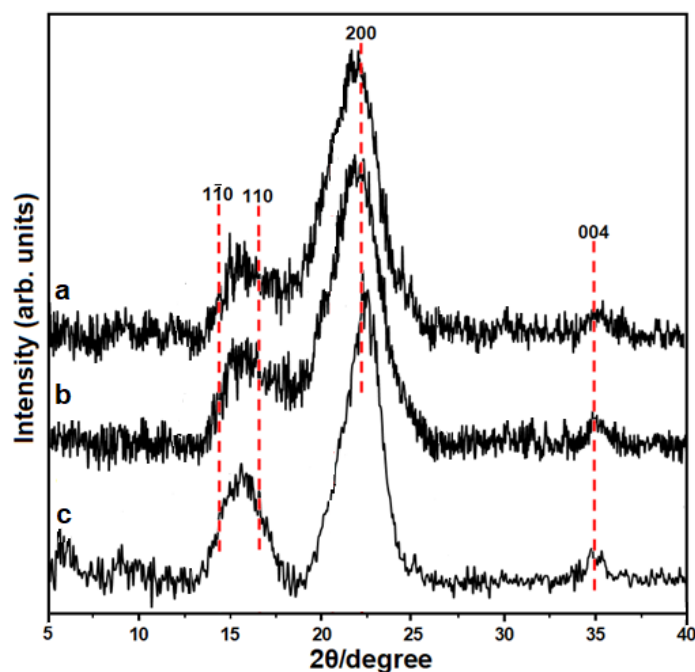


Figure 1. XRD of (a) RS (b) DRS and (c) CF.

3.2. Fourier-transform infrared spectroscopy (FTIR)

FTIR of RS, DRS and CF are indicated in figure 2 a-c, respectively. As can be observed from the figure, CF was successfully extracted from RS after serial treatments including de-waxing, delignification and excretion of silica and hemicellulose. With the bleaching process, the alkali treatment on RS probably created C-H aromatic hydrogen groups. The peak at 1524 cm^{-1} (aromatic skeletal vibrations) was possibly attributed to presence of pyranose ring skeletal C-O-C bonds of cellulose. This peak showed the delignification as its intensity decreased after each treatment that the alkali treatment caused removing the peak. Figure 6c probably showed leaching of the hemicellulose at 1750 cm^{-1} (carbonyl stretching) and removal of silica (Si-O-Si stretching) at 760 and 491 cm^{-1} . As was seen in the Figure 2c, the peaks at 3352 , 2891 and 1100 cm^{-1} could demonstrate the stretching vibrations of -OH groups, C-H stretching and cellulose structure, respectively [11]. In the anomeric region ($950\text{--}700\text{ cm}^{-1}$), the minor peak at 887 cm^{-1} was pronounced for CF (figure 2c), showing the glycosidic $\text{-C}_1\text{-O-C}_4$ deformation property of the β -glycosidic bond in cellulose [12]. This probably showed the successful CF isolation process. The CF yield from RS was achieved up to 35% which was almost similar to the result from different studies [13, 14]. Worth nothing to mention that FTIR patterns were similar for cellulose before and after delignification which could show high structural stability with no main damages to cellulose structure [15-18].

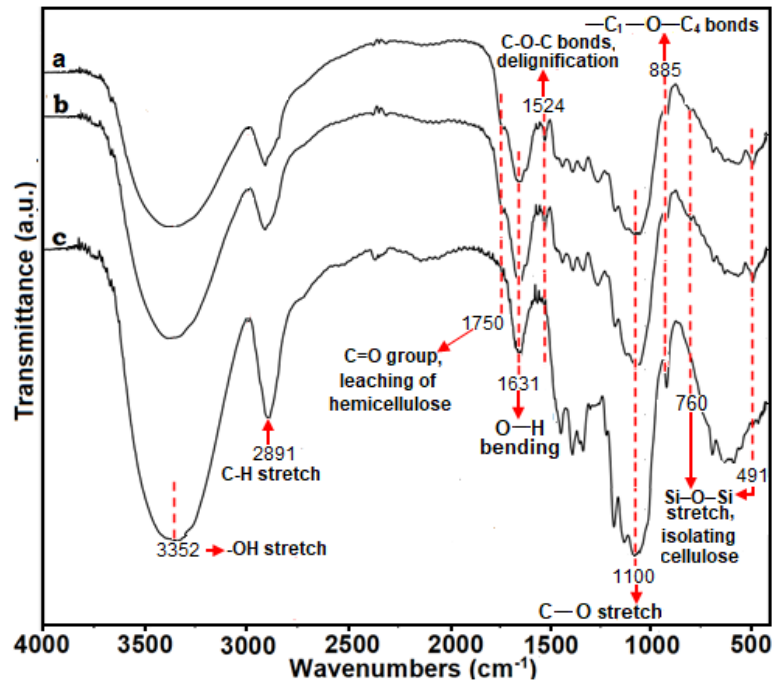


Figure 2. FTIR of (a) RS, (b) DRS, (c) CF.

3.3. Zeta Potential

The suspensions of CF indicated negative zeta potential of -33.61. These results suggested that CF has a good stability in aqueous solution [19]. The colloidal suspension with good stability was resulted from the great electrostatic repulsion that occurred among the fibers.

3.4. The scanning electron microscope (SEM)

SEM images of CF is indicated in figures 3. As ratio of hemicellulose and lignin were reduced, size of fiber gradually decreased by applying dewaxing and delignification treatments. Therefore, CF was smaller with better organized structure compare to DRS. Figure 3b shows that CF is mostly comprised cellulosic fibrils with order and disorder structure[20]. In nature, each fiber contains several to hundreds of microfibrils with the manner of adjusting together for providing cellulosic structure [15]. Subsequently, the strong hydrogen bonds between each fiber can be observed [21]. CF contained carbon, oxygen and silicon, while, RS contains high amount of silicon, but it was replaced by oxygen and carbon after the successful dewaxing and alkaline treatments [22]. The treatment on RS caused dissolving of the silica in aqueous ion and subsequently replaced by carbon, introducing improvement of crystallinity and surface area of the extracted CF [22]. From figure 3a, some pores can be seen on the surface area of the CF. CF compared to RS, it has more mesopores, and better uniform pore structure. The porosity on the surface area of CF allowed water and hydrophilic drug penetration into the fiber for its using in drug carrier application.

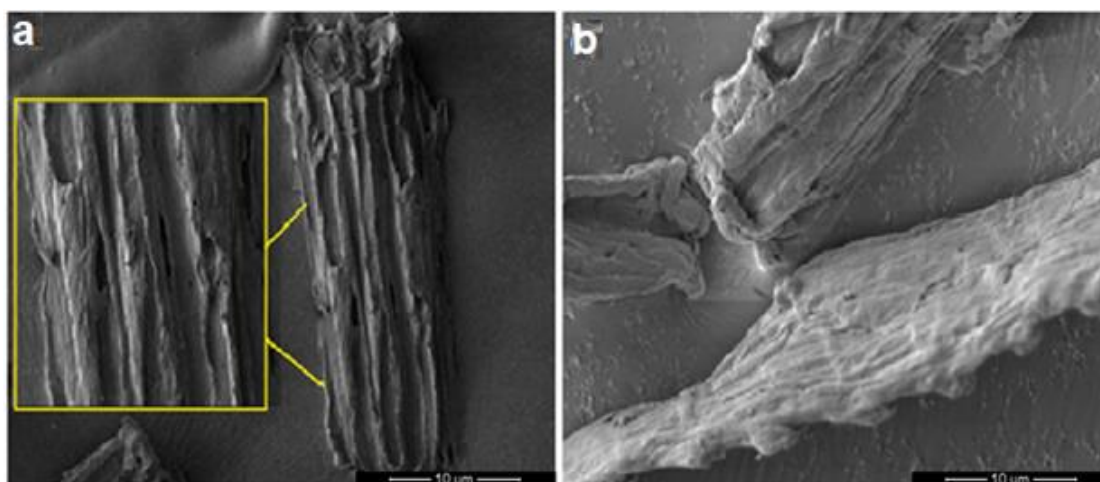


Figure 3. SEM of CF

4. Conclusion

In this study, a facile and eco-friendly method of alkali treatment was used to isolate CF from RS. Physicochemical properties of RS, DRS and CF were systematically evaluated. The XRD analysis of RS after each treatment displayed removal of unwanted substances including lignin to obtain CF with high purity and crystallinity. FTIR results exhibited gradual and parallel shifting and intensity of peaks by the treatments, proving successful bleaching and delignification process. High negative zeta potential of -33 mV proved the colloidal stability of the CF in aqueous solution. SEM images illustrated CF with organized structure. Therefore, this research showed potential of CF isolation from RS. In further study, CF will be used in drug delivery system for cancer therapy.

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