

# The functional properties of Cellulose of Wheat offal (*Tricium aestivum*) on acetylation

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**Abstract**— Functional group modification of cellulose is very important to explore new applications for cellulose. In this study, acetic anhydride was used to modify the hydroxyl groups of cellulose. Cellulose acetate (CA) was prepared from cellulose isolated from wheat offal (WO) by esterification using acetic anhydride concentrations (0.112–0.518 M), pH (9.0–13.0), time (20–70 min) and temperature (30–100 °C) respectively. Fourier Transfer Infrared Spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques used to characterise the cellulose and cellulose acetate. The optimum conditions for acetylation were found to be concentration 0.305 M (DS 0.11), pH 12 (DS 0.27), temperature 60 °C (DS 0.30) and time 50 min (DS 0.11). FTIR spectrum showed the conversion of cellulose to cellulose acetate. XRD showed the crystalline pattern of cellulose and amorphous nature of cellulose acetate. SEM images showed smooth structure of cellulose while that of the cellulose acetate had a rough surface. Thus, the results showed a non-tedious method for isolation of cellulose and conversion of the WO cellulose to high quality cellulose acetate that can find various uses in the textile, biomedical and pharmaceutical industries.

**Index Terms**— cellulose, cellulose acetate, esterification, optimum conditions, SEM, XRD, Wheat offal

## 1 INTRODUCTION

Lignocellulosic biomass is the most abundant renewable biomass on the earth with a worldwide yearly supply of approximately 200 billion tones [1], [2]. Lignocellulosic biomass comprising forestry, agricultural and agro-industrial wastes are inexpensive and relatively carbon-neutral source of energy [3]. An intense research scrutiny is currently undertaken worldwide to identify attractive chemical transformations to convert biomass into organic chemicals and to develop economically feasible processes for these transformations on a commercial scale [4].

Cellulose is a polysaccharide made of anhydrous D-glucose units connected together via  $\beta$ -1,4-glycosidic bonds and is a promising raw material for producing important chemicals, including cellulosic-ethanol, hydrocarbons, and starting materials for the production

of polymers [5], [6]. The production of cellulose derivatives has extensive interest worldwide, mainly because of its abundance in nature, its biodegradability and its lower environmental impact in comparison with polymers obtained from fossil sources [7]. Nowadays derivatives of cellulose have been widely used in waste treatment, oil recovery, paper manufacturing, textile finishing, food additives and pharmaceutical application [8].

Nigeria is well-endowed with rich and renewable natural tropical forest resources. Cellulose based polymer can be used to reduce the use of the limited fossil resources in Nigeria with its environmentally-friendly properties for industrial applications. However, cellulose application is limited because it cannot be formed easily into a desired shape and it cannot be dissolved in a cheaper and more common solvent due to the presence of hydrogen bonds in the structure. However, to increase its applicability, the functional groups of the cellulose are modified to other derivatives that are more soluble through chemical derivatization reactions [9].

Cellulose acetate as an important derivative of cellulose is estimated annually to be 1.5 billion pounds being manufactured globally [10]. It has a vast industrial applications such as coatings, cigarette filters, textile fibers, consumer products, filtration membranes,

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composites, laminates, and medical and pharmaceutical products [11], [12], [13].

Many researchers have reported the isolation of cellulose from agricultural wastes and subsequent conversion to different derivatives of cellulose. The agricultural wastes includes palm kernel cake [14], rice husk [15], sugar beet pulp [16], cavendish banana pseudo stem [17], cashew tree gum [18], Mimosa pigra peel [19], orange peel [20], papaya peel [21] and [22] respectively.

However, little or no work has been done on the isolation of cellulose from WO and subsequent modification to cellulose acetate with optimization of reaction conditions. Hence, this present paper focuses on the preparation and characterization of cellulose acetate from agricultural waste.

## 2 MATERIALS AND METHODS

### 2.1 Materials and Chemicals

Wheat offal (*Tricicum aestivum*) used in the study was obtained from Alaba International market, Ojo town, Lagos state. WO was extensively washed with distilled water to remove impurities (mainly dust). The materials were first dried in sunlight and cut into smaller pieces and milled to pass through a 1–2 mm mesh. The milled sample was then stored at room temperature. The reagents and chemicals used in this study were of standard analytical grades.

### 2.2 Isolation of cellulose from wheat offal

Isolation of cellulose from wheat offal was carried out by methods previously used by [23], [24], [25], with modifications. 800 g of the agricultural waste material was weighed inside the steel reaction vessel and soaked with water for 24 h. The material was filtered and washed thoroughly with distilled water until filtrate became clear. The material was then boiled in water for 1hr, followed by filtration and washing with distilled water until filtrate became clear. 3.0L of 3.5% HNO<sub>3</sub> and 2.0L of Na<sub>2</sub>SO<sub>3</sub> previously prepared, were poured inside the vessel containing the material and the reaction proceeded for 2.5 h at 90°C with constant stirring, followed by filtration and washing with distilled water until filtrate became neutral to blue and red litmus papers. Further delignification process continued with the addition of 2.0 L of 2% NaOH and 2.0 L of 2% Na<sub>2</sub>SO<sub>3</sub> at 80°C for 2 h under constant stirring followed by filtration and washing with distilled water until filtrate became neutral to both blue and red

litmus papers.

Final delignification process by alkali hydrolysis was done by addition of 3.0 L of 17.5% NaOH to the material under constant stirring for 2.5 h at 70°C. This was followed by filtration and washing with distilled water until filtrate became neutral to blue and red litmus papers. Finally, the material was bleached with 3.5% NaOCl<sub>2</sub> for 45min under constant stirring at 50°C followed by washing until filtrate became clear and neutral to red and blue litmus papers. The final product obtained was air-dried, milled into fine powder material and stored in dried container.

### 2.3 Acetylation of Cellulose

Acetylation of cellulose was carried out accordingly to previous methods by [26], [27], with modifications to cause platicization of the lignocellulosic fibre and improve on the functionalities of the isolated cellulose from WO. 15 g of well powdered and previously dried cellulose were dispersed in 75 ml of distilled water ratio (1:5) and stirred to homogenous slurry. The pH of the slurry was adjusted to 9.0 using 1M NaOH solution. 0.112 M of acetic anhydride was added under magnetic stirrer at 30°C for 20 min while maintaining the pH at 9.0. At the end of 20 min, the reaction was stopped and the product obtained was washed thoroughly with distilled water until filtrate became neutral to both blue and red litmus papers. The product was air-dried at room temperature for 48 h. This reaction process was repeated to investigate the effects of temperature; (30, 40, 50, and 60)°C, time (20, 30, 40, and 50) min, pH (9.0, 10.0, 11.0, and 12.0) and concentration (0.183, 0.244 and 0.305) M respectively.

### 2.4 Determination of Degree of Acetylation

The method [28], was used for the determination of the degree of acetylation of the acetylated cellulose from wheat offal. 5.0 g of the acetylated cellulose was weighed into a 250ml flask and 50ml distilled water was added. Upon mixing, two drops of phenolphthalein indicator were added and the suspension was titrated with 0.1 M Sodium Hydroxide solution to obtain permanent pink end point. Furthermore, 25ml, 0.45 M Sodium Hydroxide solution was added and the flask was sealed tightly with a rubber stopper and shaken vigorously for 30mins. After shaking, the stopper was removed carefully and then washed thoroughly together with the walls of the flask with distilled

water. The saponified mixture, containing excess alkali was then titrated with 0.2 M HCl solution until disappearance of the phenolphthalein colour. The isolated cellulose (unmodified) was treated in the same manner to obtain blank value.

Percentage acetyl (dry basis)

$$= \frac{(\text{blank titre} - \text{sample titre}) \text{ ml} \times \text{acid molarity} \times 0.043 \times 100}{\text{sample weight in g (dry basis)}}$$

$$\text{Degree of substitution (D.S)} = \frac{162A}{4300 - 42A}$$

Where A = percentage of acetyl (dry basis)

## 2.5 CHARACTERIZATION OF THE CELLULOSE AND CELLULOSE ACETATE

### 2.5.1 Fourier Transform Infrared (FT-IR) Spectroscopy

Samples used were oven dried (60°C) for 1 hr to remove moisture contents and 0.2 mg was weighed, powdered and used for the measurement. The functional groups present in the isolated cellulose acetate prepared were determined and confirmed using Automated Bruka Fourier Transform Infrared Spectrophotometer (without KBr) in the wavelength range 4000-400 cm<sup>-1</sup>.

### 2.5.2 Morphological analysis by scanning electron microscope (SEM)

The surface analysis of isolated cellulose and cellulose acetate prepared were characterized using Jeol JSM-6380A SEM. The two dried powdered samples of isolated cellulose and cellulose acetate were coated using gold (Au). Images were taken at 10 kV voltage mapping. The dimension of the powdered isolated cellulose and prepared cellulose acetate samples were taken between the range of 200 µm and 30 µm at magnification x1000 respectively.

### 2.5.3 Determination of crystallinity of isolated cellulose and cellulose acetate prepared by X-ray diffraction technique

The crystalline nature of isolated cellulose and cellulose acetate prepared from wheat offal were determined using X-Ray diffractometer Philip – PW 1011 model. The X-Ray patterns were measured by using CuKα as radiation source by supplying 40 kV and 40 mA to X-ray generator. The patterns were recorded at 2θ from 10° to 60°.

## 3 RESULTS

### 3.1 Percentage yields

The acidified (nitric acid) alkali treatment of wheat offal produced 47.4% yield of cellulose which was white in colour.

### 3.2 Degree of Substitution

#### 3.2.1 Degree of substitution with varying pH

The degree of substitution increased with increase in the pH values up to the optimum condition of pH 11.0 followed by decrease in the degree of substitutions. (Figure 1). Degradation occurred after DS value of 0.27 was attained as a result of the medium tending towards high alkalinity and which does not favour the acetylation reaction.

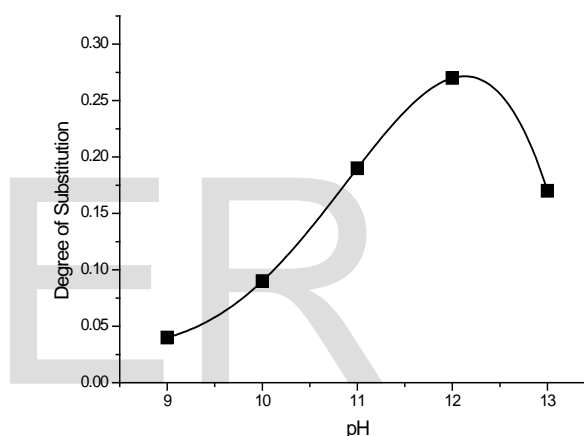


Figure 1: Degree of substitution with varying pH

#### 3.2.2 Degree of substitution with varying time interval

The degree of substitution increased with increase in the period of acetylation up to the optimum condition time at 50 mins (DS 0.11). After the optimum condition time, there was gradual decrease in the degree of substitution. (Figure 2). This observation is due to prolonged reaction time which resulted in the formation of gel instead of slurry and which is difficult to filter and thus form rubbery material when dried inside the oven. This result is consistent with earlier work reported by [29], [30].

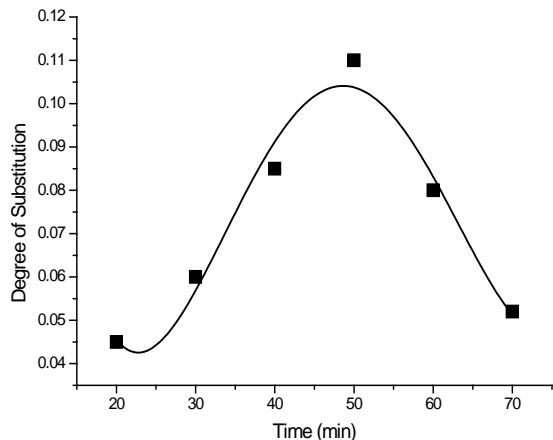


Figure 2: Degree of substitution with varying time interval

### 3.2.3 Degree of substitution with varying temperature

From Figure 3, as the temperature increased, the degree of substitution also increased up to the optimum temperature at 80 °C after which decrease in the DS values were observed at temperatures above the optimum condition. This shows that the functional groups of the CA as well its molecular structure have been altered which is similar to previous work reported by [30], [31].

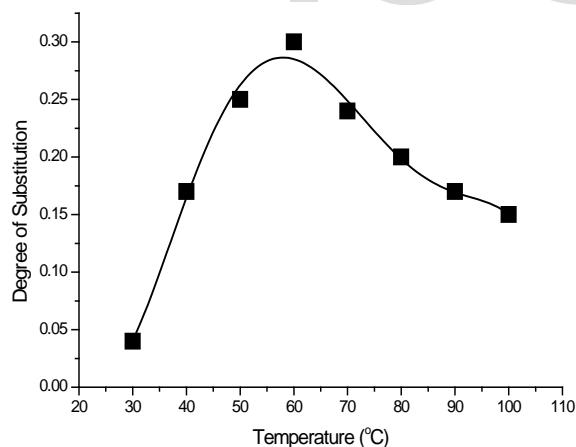


Figure 3: Degree of substitution with varying temperature

### 3.2.4 Degree of substitution for varying concentration

As shown in Figure 4, the concentration of acetic anhydride as the acetylating agent is very important in the production of cellulose acetate and therefore, studying the effects at varied concentration is important. The DS of cellulose increased with increase in concentration of acetic anhydride until 0.305 M concentration after which the DS started decreasing. This is due to the reacting medium being more acidic and which does not favour the production of cellulose acetate. Similar observations were reported by [12], [30].

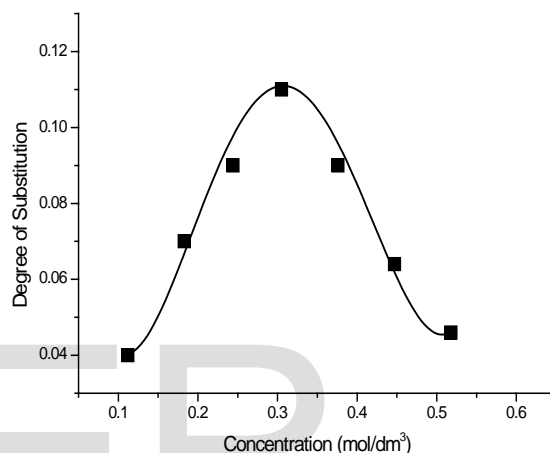


Figure 4: Degree of substitution with varying concentration

## 4 DISCUSSIONS

### 4.1 FT-IR spectroscopy

The functional groups of cellulose isolated from WO and the acetylated cellulose were examined using FT-IR spectroscopy. The FTIR spectra of the isolated cellulose and CA prepared showed typical characteristic wavelength of OH broad absorption band, C-H stretching vibration, C-C-C bending, -COO of ester group and C=O stretch of the acetyl group. Figure 5 shows the FT-IR spectra of the isolated cellulose and cellulose acetate prepared. The broad bands in the regions between  $3439\text{ cm}^{-1}$  is due to the OH-stretching vibration in the isolated cellulose which gives considerable information about the hydrogen bonds. The absorption bands between  $1040\text{ cm}^{-1} - 1150\text{ cm}^{-1}$  is due to the C-O-C ring skeletal vibration which is similar to previous work reported [32]. Also, the peaks between the regions  $2800\text{ cm}^{-1} - 3000\text{ cm}^{-1}$  show the asymmetric stretching of  $\text{CH}_2$  bond while the peaks around  $1635\text{ cm}^{-1}$  indicate the water absorption band which is

similar to previous work earlier reported [33].

The absorption bands between the regions  $3400\text{ cm}^{-1}$  –  $3500\text{ cm}^{-1}$  represent the OH-stretching vibration in the acetylated cellulose. The bands between the regions  $1735\text{ cm}^{-1}$  –  $1755\text{ cm}^{-1}$  in the cellulose acetate is due to the C=O stretching of the acetyl group which indicates that acetylation occurred in the cellulose. The absorption bands between  $1040\text{ cm}^{-1}$  –  $1150\text{ cm}^{-1}$  are due to the C-O-C ring skeletal vibration which has also been reported by [32]. The peaks observed between the regions  $2800\text{ cm}^{-1}$  –  $3000\text{ cm}^{-1}$  show an asymmetric stretching of  $\text{CH}_2$  bond. Peaks observed at  $1635\text{ cm}^{-1}$  indicate the water absorption bands also reported [33].

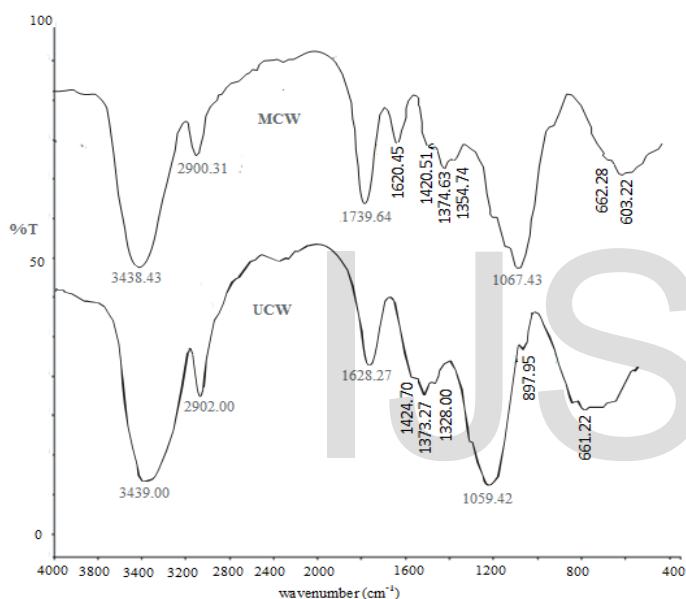


Figure 5: FTIR spectra of unmodified cellulose (UCW) and modified cellulose of Wheat offal

#### 4.2 SEM analysis

The scanning electron micrographs of isolated cellulose and Cellulose acetate are shown in Figure 6 (a) & (b) respectively at specific magnifications. At higher concentrations, the cellulose is completely elongated with fibrils of various thicknesses and lengths. Similar observation [34] has been reported. This is because during acetylation of cellulose, the intra and inter molecular hydrogen bonds of cellulose are easily broken. Also, the bonds between the polyhydroxyl groups of the polysaccharides are weakened; resulting in the swelling of the cellulose and thus the fiber shows different increase in length. Surface analysis of the cellulose by SEM showed that the packed structures of the fibrils were not completely separated from each other

and thus, cluster of particles were formed. Meanwhile, the SEM micrograph of the cellulose acetate at higher magnifications (x1000) shows that cellulose acetate had a woven surface like a fiber with a completely elongated fibrils resembling particle of atoms not closely packed together to form cluster. The fibrils are completely separated from each other.

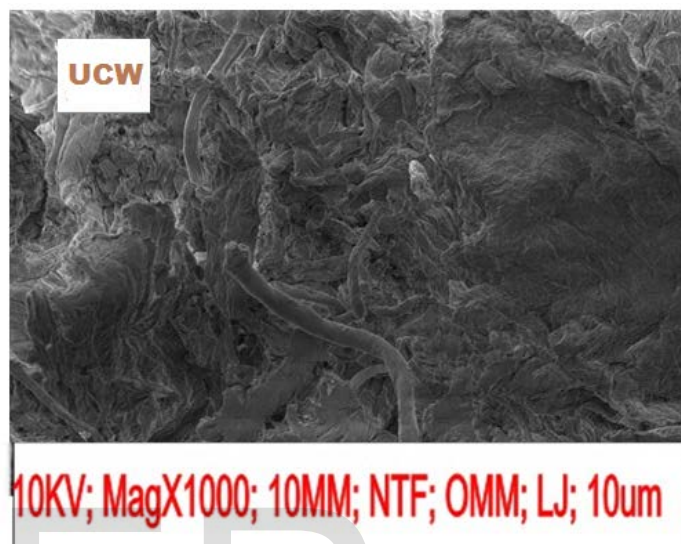


Figure 6 (a): SEM micrograph of unmodified cellulose of wheat offal.

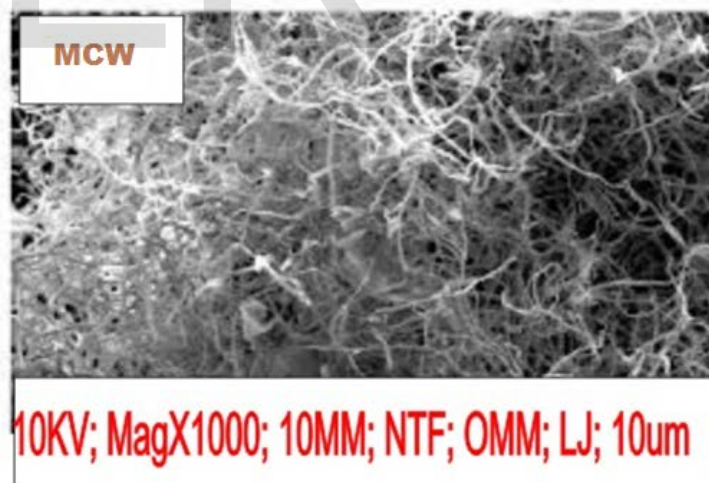


Figure 6 (b): SEM micrograph of Modified cellulose of Wheat offal.

#### 4.3 X-Ray Diffraction (XRD)

XRD analyses of isolated cellulose and CA were done to determine the structural and chemical changes of the isolated cellulose CA respectively. Cellulosic fibres consist of three major components namely Lignin, Hemicellulose and cellulose. Cellulose shows crystalline nature while lignin and hemicellulose, are

amorphous in nature. Hence, the crystallinity of the fibres is expected to decrease after acetylation.

The diffractograms of isolated cellulose from Wheat offal showed the diffraction intensity at  $22.0^\circ$  and a shoulder peaks in the regions  $2\theta = 15^\circ, 25^\circ, 30^\circ$  which indicates the presence of cellulose while the acetylated cellulose exhibits diffraction intensity at  $21^\circ$  and lower intensities of  $2\theta = 11.4^\circ, 25^\circ$  and  $30^\circ$ , similar to previous work reported [35]. The sharp peaks observed for the isolated cellulose are due to its crystalline nature. The lower peak intensity of the acetylated cellulose as shown in figure 7 (b) indicates the complete removal of non-cellulose due to alkaline hydrolysis and acetylation respectively. Thus, the inter fibrillar regions are likely to be more dense and more rigid and thereby make the fibrils more capable of rearranging by themselves similar to earlier work reported [36].

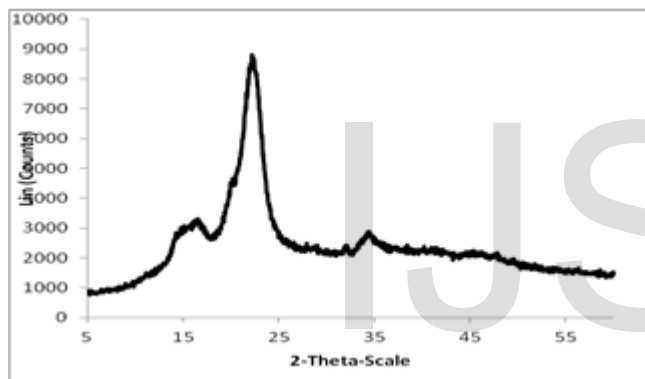


Figure 7 (a): X-ray diffraction pattern of isolated cellulose

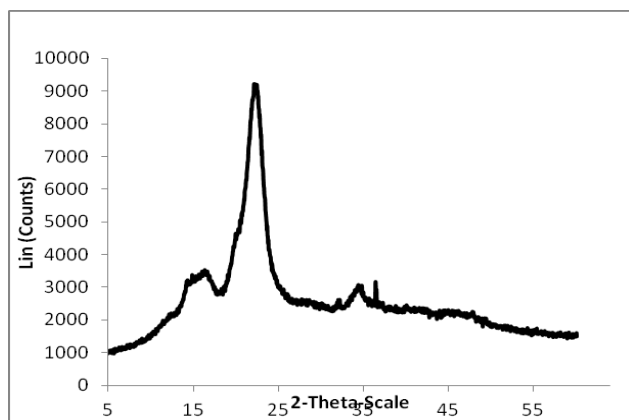


Figure 7 (b): X-ray diffraction pattern of Cellulose acetate

## 5 CONCLUSION

In this research work, cellulose was successfully isolated from wheat offal by alkali hydrolysis and percentage yield was 47.2%. The cellulose was converted to cellulose acetate (CA) by acetylation with acetic anhydride at various time intervals, pH, concentration and temperature respectively. Optimum conditions for the preparation of cellulose acetate were determined.

FTIR spectra revealed the conversion of cellulose to cellulose acetate between wavenumbers  $1735 - 1755 \text{ cm}^{-1}$  which indicate the presence of carbonyl groups (C=O). Furthermore, SEM and XRD also revealed modification of the cellulose to cellulose acetate.

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