Preparation and characterization of corn cob cellulose acetate for potential industrial applications

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ABSTRACT

Background: Locally generated biopolymers are amenable to further processing to widen their industrial applications. The study was aimed at generating low-cost cellulose acetate from corn cob residue and its characterizations for potential applications in biopolymer industries.

Methods: Cellulose was extracted from the corn cob residue using the sodium hydroxide method. Acetylation of the cellulose to obtain corn cob cellulose acetate was carried out by adding appropriate quantities of a glacial acetic and acetylating mixture of acetic anhydride and sulphuric acid. The corn cob native cellulose and corn cob cellulose acetate were characterized using scanning electron microscopy (SEM) to examine their morphology, Fourier-transform infrared spectroscopy (FTIR) and powder X-ray diffraction (XRD) for structural elucidation while differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were employed to investigate their thermal properties.

Results: - Two corn cellulose acetate samples with degree of substitutions 1.87 and 2.65 for samples CDA and CA respectively were obtained. They had improved solubilities in some organic solvents compared to the corn cob cellulose. The SEM examination showed the surface of the corn cob native cellulose (NC) was smooth and had a regular bundle-like structure while acetylation destroyed the original cellulose structure. Cellulose acetate samples showed a cluster-like structure with different sizes and a rough flake-like surface. FTIR and XRD studies showed that acetyl groups substituted cellulose hydroxyl groups. While FTIR study showed that the cellulose acetates had sharp bands between $1728\ cm^{-1}$ to $1733\ cm^{-1}$ and around $1368\ cm^{-1}$ wavenumber unlike the corn cob cellulose sample, the data generated from XRD study indicated that acetylation of the corn cob cellulose led to 47% and 77% decrease in the crystallinity of CDA and CA samples respectively. The thermal analysis data from DSC and TGA studies confirmed that the acetylation improved the corn cob cellulose's thermal stability as indicated by the degradation of cellulose acetate samples at higher temperatures.

Conclusion: The study concluded that low-cost cellulose acetate generated from corn cob residue could be potentially employed as a renewable, biodegradable, biocompatible polymer for industrial applications

1.   Introduction

Polymers have been employed in the drug delivery system (DDS) for delivering various therapeutic agents. It can be divided into natural, synthetic, biodegradable, and non-degradable polymers. Natural polymers are currently gaining attention in the drug delivery system over synthetic polymers due to their biodegradability, renewability, biocompatibility, relatively low cost, and low immunogenicity, among other advantages.[1] The versatility of the synthesis and formulation of biopolymers provide advantages in terms of their industrial applications. Biopolymers can be easily degraded to non-toxic substances and excreted by physiological pathways.

Cellulose acetate, a cellulose derivative, is one of the important biopolymers obtained by the acetylation of cellulose. It has been considered for many applications because of its excellent physical, chemical, and biological properties.[2] Cellulose which is composed of β-1,4-anhydrous-D-glucopyranose units, has highly reactive hydroxyl groups that acetyl groups can substitute to form

cellulose acetate.[3] Cellulose is the most abundant natural polymer, which can be found in plants, bacteria, marine animals, algae, fungi, and minerals. The excellent properties of this cellulose which include degradability, scalability, biocompatibility, renewability, and profitability, amongst others have been reported in the literature.[4] However, unmodified cellulose is insoluble in common solvents limiting its industrial applications.[2] Cellulose acetate is more amenable to further processing and has wider industrial applications, including its fabrications as nanofibers via electrospinning techniques.[5]

Commercially, cellulose is mostly obtained from hardwoods, which are more expensive than other lignocellulosic materials. Agricultural residues are lignocellulosic materials which are alternative sources of cellulose. Billions of tons of these residues are produced annually, and the current disposal system of these residues constitutes a nuisance to the environment.[6] Nowadays, researchers are focusing on using abundant and inexpensive industrial residues as sustainable industrial feedstocks. The valorization of agricultural residues is a major global issue.

Corn is one of the most important cereal crops with estimated global production to reach 1,177.3 million metric tons in 2023.[7] The estimated compound annual growth rate (CAGR) is 2.14%.[7] Corn cob is a processing residue from corn; unlike most common agricultural residues, corn cob is difficult to recycle as feed or fertilizer. Most often, they are either left to dry on the farm, after which they are burnt off or found littering everywhere.[8] The composition of corn cob fiber is similar to wood; hence it can be used as a wood substitute.[6] Although an attempt is being made for the introduction of various industrial valorization techniques for corn cob residue, its use is still very low. Hence most of the generated corn cob residue is disposed of.[9] Utilization of this lignocellulosic residue as a source of cellulose has been reported by several authors.[10,11,12] However, there are limited studies on the preparation and characterization of cellulose acetate obtained from corn cob residue.

In the study, we report the preparation of low-cost cellulose acetate polymer from lignocellulosic corn cob residue The obtained cellulose acetates were characterized using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

2. Materials and Methods

2.1 Materials

Sodium hydroxide (NaOH) pellets (Analar grade 97% MCR-21720, Molychem, Mumbai), Glacial acetic acid (CH₃COOH) (Analar grade, batch NO; 730918, Central drug house Ltd, New Delhi, 1.7% Sodium chlorite (NaClO₂) (Analar grade 80%, MCR-20344, Molychem, Mumbai, India), Acetic Anhydride (CH₃CO)₂O (Analar grade, CAS-No;64-17-5, Merck, Germany) and Chloroform (Merck, Germany) were used in the study.

2.2 Methods

2.2.1 Extraction of cellulose from Corn cobs

The corn cob residues (2 kg) collected from rural farmers were air-dried for seven days prior to oven drying at 50ºC for 24 h. The method of cellulose preparation reported in a previous study was adopted with some modifications.[13] The milled and oven-dried powdered corn residue (500 g) was mixed with 5 L of 2% NaOH, and the mixture was heated to 100ºC for 2 h. It was filtered, and the residue was mixed with 4 L of 17.5% NaOH, heated at 100ºC ± 10ºC for 45 min, filtered, and washed thoroughly. The cellulose was bleached with 1 L of 6.25% Sodium hypochlorite at 80ºC for 1 h. The bleached material was washed repeatedly with distilled water and then air-dried for seven days to obtain the corn cob native cellulose (NC).

2.2.2 Acetylation of Corn cob cellulose

Acetylation of corn cob cellulose (NC) was carried out as described in a previous study with few modifications.[14] Briefly, the modification was achieved by mixing 2 g of the cellulosic material (NC) with 35 mL of glacial acetic acid and heating with a Stuart heat stir machine at 55ºC for 1 h. An acetylating mixture of 10 mL of acetic anhydride and 0.4 mL concentrated sulphuric acid (catalyst) was gradually added to the glacial acetic acid–pulp mixture. The resulting mixture was kept in a water bath for 1 h at 55ºC with continuous stirring until a clear solution was obtained. The mixture was divided into two equal parts; one part was poured into 1000 mL of the distilled water with stirring. The precipitate was filtered and thoroughly washed to obtain the cellulose acetate sample (CA), while for the second part, 12.0 mL of acetic acid and 3.5 mL of distilled water were added with vigorous stirring and were allowed to stand for 1 h at 55 °C. The precipitate was filtered and thoroughly washed to obtain the cellulose acetate sample (CDA).[14]

2.2.3 Degree of substitution

The degree of substitution (DS) for the corn cob cellulose

acetates (CA and CDA) was determined through a saponification reaction described by Rodrigues *et al*.[15]

2.2.4 pH and Solubility

The pH and solubility (water and organic solvents) of the corn cob native cellulose, corn cob cellulose acetates and commercial brand of cellulose acetate were evaluated. The pH of 10% slurry of the powder samples was determined using a pH meter (H12211 pH meter Hanna Instruments, USA), while the solubility of the samples was determined in water, chloroform, acetone, acetic acid, formic acid and ethanol. 1g of powder samples was dissolved in 10 mL of the solvent.

2.2.5 Morphological Characterization

The morphology of the powders was observed using scanning electron microscope (SEM). The SEM micrographs were photographed by a ZESS EVO HD 15 scanning electron microscope (Cari Zeiss NTS Ltd, Cambridge, UK). The samples were first mounted with Agar Scientific G3347N carbon adhesive tab on Agar Scientific G301 0.5" aluminium specimen stub (Agar Scientific Ltd., Stansted, UK) and photographed at a voltage of 10.00 kV. The manual sputter coating S150B was used for the gold sputtering of SEM samples. The thickness of the gold coating was 15 nm.[16]

2.2.6 Structural Characterization

The FTIR spectra of the solid samples were measured using an ALPHA interferometer (Bruker UK Limited, Coventry, UK) equipped with a horizontal universal attenuated total reflectance (ATR) accessory. For each sample, an average of 30 scans was collected per spectrum with a resolution of 2 cm^{-1} in the spectral region of 400 to 4000 cm^{-1} using the OPUS software at room temperature.[16]

Powder X-ray diffraction patterns of solids were recorded from a range of 2 - 80° (2θ) at a scanning rate of 0.4° (2θ) min^{-1} by a D2 PHASER diffractometer equipped with LYNXEYE XE-T detector (Bruker UK Limited, Coventry, UK). Cu-Kα radiation was used with a voltage of 30 kV and a current of 10 mA.[16] The measurements from the machine were analysed using Diffraction Eva software.

2.2.7 Thermal Properties

A NETZSCH DSC 214 Polyma (NETZSCH instrument, Wolverhampton, UK) operated under a nitrogen atmosphere measured the DSC analysis of solids. The instrument was calibrated using indium metal. A 4 – 8 mg sample was analysed in an aluminium pan with a pierced pinhole lid. Measurements were carried out at a heating rate of 20°C/min with a temperature range of 40 to 400°C.[16]

The TGA analysis was carried out at a heating rate of 20°C/min from 30 to 700°C using thermogravimetry NETZSCH TG 209 F3 Tarsus (NETZSCH instrument, Wolverhampton, UK).

2.3 Statistical Analysis

The mean comparison of the test samples with the standard was evaluated using a one-way analysis of variance. The Tukey test determined significant differences ($P < 0.05$). OriginPro® 8.5 software (OriginLab® Corporation Northampton, MA 01060 USA) was employed for statistical evaluation.

3. Results

The percentage yields of corn cob cellulose, cellulose acetates CA and CDA were 25 %w/w, 40.4 %w/w and 29.4 %w/w with respect to the corn cob residue. Degree of substitutions (DS) of the corn cob cellulose acetates CA and CDA were 2.65 ± 0.41 and 1.86 ± 0.17, respectively. The cellulose powders were either white or yellowish white granules in appearance. The pH and solubility of the corn cob native cellulose (NC), the corn cob cellulose acetates (CA, CDA) and commercial cellulose acetate (CCA) were evaluated. The pH for NC, CA, CDA and CCA were 5.0±0.5, 3.6±0.5, 3.7±0.8 and 4.3±0.5 respectively. All the cellulose samples were practically insoluble in water and ethanol, while the acetylated cellulose samples were slightly soluble or soluble in some organic solvents (acetic acid, formic acid, acetone, and chloroform) used.

3.1 Morphological Characterization

The SEM micrographs of the corn cob native cellulose and cellulose acetate samples are shown in Figure 1.
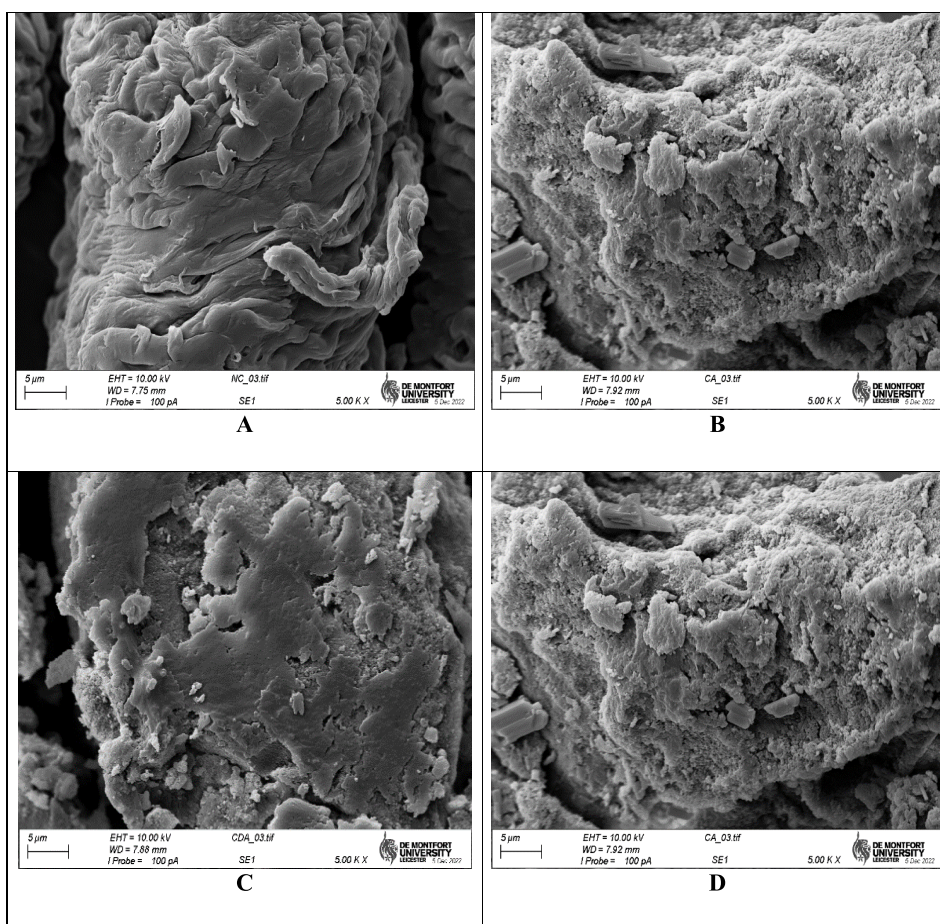
Figure 1 SEM images (magnification 5.00KX) of A, Corn cob native cellulose (NC), B. Corn cob cellulose acetate (CA), C, Corn cob cellulose acetate (CDA) and D, Commercial brand of cellulose acetate (CCA)

3.2 Structural Characterization

Fourier Transform Infrared Spectroscopy (FTIR) and powder X-ray diffraction (PXRD) were employed for the structural characterization of the cellulose samples. The FTIR spectra for the cellulose samples are shown in Figure. 2, while their PXRD diffractograms are in Figure. 3. The proportion of the crystalline and amorphous parts of the cellulose samples was generated from the PXRD diffractograms using Diffrac Suite Eva software and results presented in Table 1.
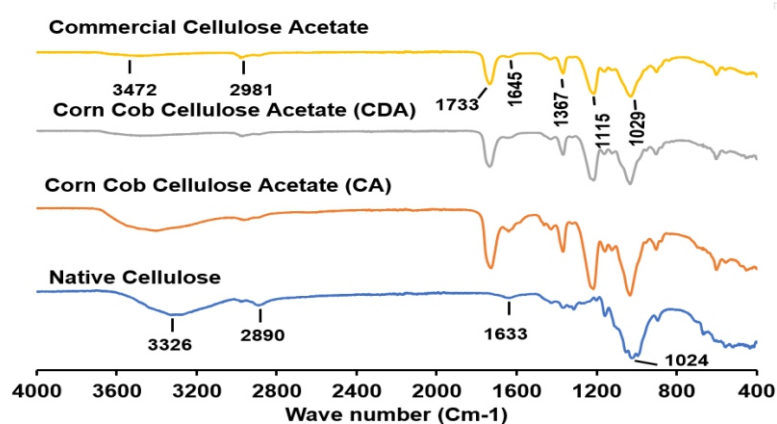
Figure 2. Normalized FTIR spectra of native corn cob cellulose (NC), corn cob cellulose acetates (CA. CDA) and commercial brand cellulose acetate (CCA) powders.
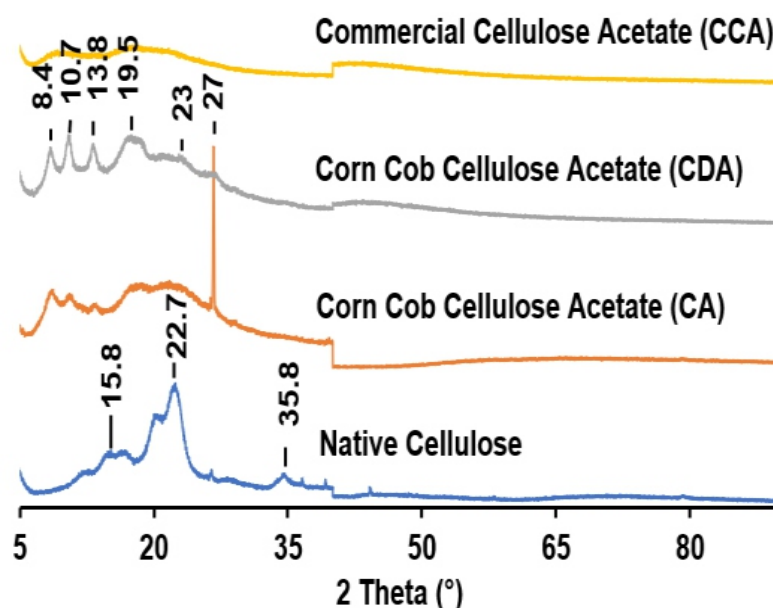

Figure 3. XRD diffractograms of native corn cob cellulose (NC), corn cob cellulose acetates (CA, CDA) and commercial brands of cellulose acetate (CCA)

Table 1 Degree of Crystallinity generated from the XRD diffractograms

Sample Code	Crystallinity (%)	Amorphous (%)
NC	42.8	57.2
CA	29.3	70.7
CDA	22.4	77.6
CCA	10.0	90.0

native corn cob cellulose (NC), corn cob cellulose acetates (CA, CDA) and commercial brand of cellulose acetate (CCA)

3.3 Thermal characterization
The thermal characteristics of the cellulose samples were determined using the Differential Scanning Calorimetry (DSC) analysis and Thermogravimetric analysis (TGA). The DSC and TGA thermograms are presented in Figures 4 and 5 respectively.
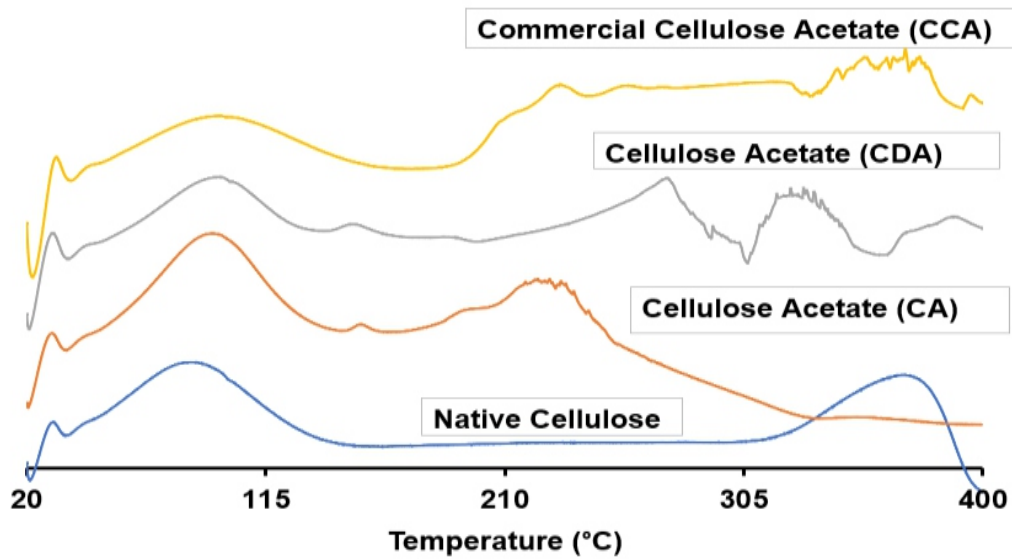
Figure 4. DSC thermograms of native corn cob cellulose (NC), corn cob cellulose acetates (CA, CDA) and commercial brand of cellulose acetate (CCA)
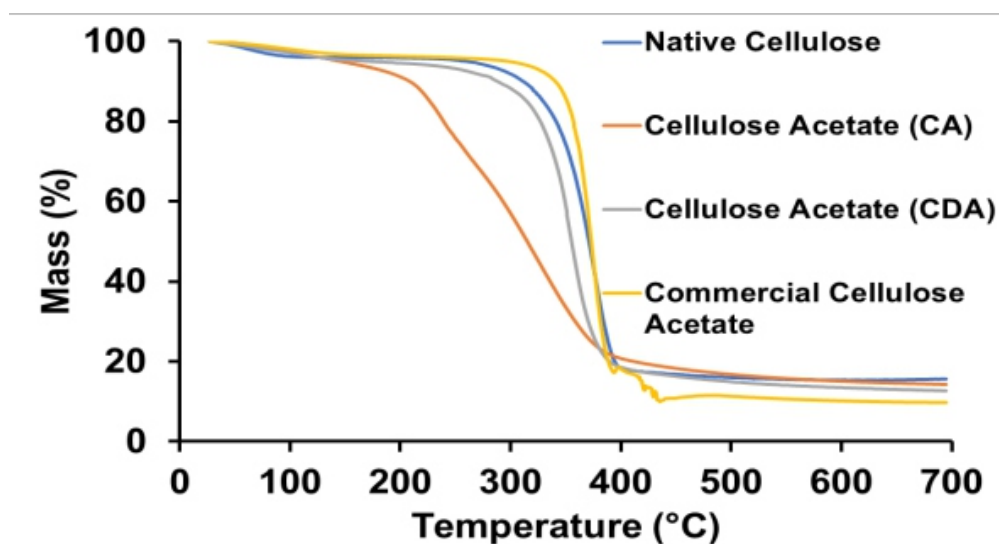

Figure 5. TGA thermograms of native corn cob cellulose (NC), corn cob cellulose acetates (CA, CDA) and commercial brand of cellulose acetate (CCA)

4. Discussion

4.1 Degree of Substitution

The degree of substitution of CDA was 1.86 ± 0.17, characterizing it as a cellulose diacetate while DS for CA was 2.65 ± 0.41, characterizing it as a cellulose triacetate.[15] During acetylation reaction, the hydroxyl groups are partially replaced by acetyl groups, the more effective the acetylation process, the more the DS.[17]

4.2 pH and Solubility

The pH of extracted corn cob native cellulose was in line with pharmacopeia standards pH (5.0-7.5) which is pH of 5.0.[18] An acidic pH observed for the cellulose acetates might be attributed to the acetic acid employed in the preparation. Acetylation is a cellulose derivatization process that greatly improves the solubility of cellulose. This is due to the replacement of the hydroxyl groups with acetyl groups, thereby disrupting the strong H-bond network.[17] The solubility of the native corn cob cellulose was improved on acetylation. Unmodified cellulose has limited applications due to its insolubility in water and common organic solvents and its solubilisation is achieved only by complex solvent systems. It was reported that cellulose acetate's solubility depends on the degree of substitution and its wide range of solubility indicates a high degree of substitution and lower crystallinity. This improved solubility indicates that cellulose acetate is amenable for further processing in biomedical and industrial applications for example, it could be employed as an electrospinning polymer for nanofibers production.

4.3 Morphological Characterization

The morphology of the samples was characterized by SEM. As shown in Figure 1, the surface of the corn cob native cellulose (NC) was smooth and had a regular bundle-like structure. This may be attributed to the aligning of the several micro-fibrils of the cellulose.[19] The SEM of the cellulose acetate samples show rough surface with loose particles like flakes or pellet-like structures, in a cluster of different sizes. The original structure of the cellulose was destroyed from a compact structure to a loose structure. The highly ordered compact structure of the cellulose makes it difficult to dissolve in organic solvents; the disruption of this structure on acetylation allows for more free energy for reaction hence this is in line with the solubility data.

4.4 Structural Characterization

The FTIR study was conducted to characterize the presence of specific functional groups in the samples. The FTIR spectra of the native corn cob cellulose (NC) and cellulose acetate samples (CA, CDA and CCA) are presented in Figure 2. The four spectra (NC, CA, CDA and CCA) showed characteristic bands and peaks of a cellulosic substance. The absorption peaks at 3326 cm^{-1}, 3400 cm^{-1}, 3485 cm^{-1} and 3472 cm^{-1} for NC, CA, CDA and CCA respectively might be attributed to the O-H stretching and it appears smaller for the cellulose acetates compared to the same peak in the spectrum for the corn cob cellulose. The high intensity of the hydroxyl groups of the corn cob cellulose sample could be associated with its high cellulose content after alkali and bleaching treatments. Similarly, strong bands around 2850-3100 cm^{-1} and 897-1165 cm^{-1} correspond to C-H stretch and designated C-O-C stretching at the β-(1, 4) glycosidic linkage characteristic of cellulosic materials.[20] However, there were some noticeable differences between the spectra of the corn cob cellulose and the three cellulose acetate samples. Unlike in the NC spectrum, there were sharp bands between 1728 cm^{-1} to 1733 cm^{-1} for the cellulose acetate samples, which can be attributed to the stretching of ester carbonyl of cellulose acetate. The appearance of this peak is a main indication that cellulose has been acetylated. The stronger band in this region for CA sample than in CDA sample is an indication that a higher degree of acetylation took place for CA than CDA sample. Secondly, sharp peak around 1368 cm^{-1} wavenumber, was observed in the spectra of the cellulose acetate samples only, it is attributed to vibration of C–H bond, which is a band characteristic of the acetyl groups. Thirdly, the strong narrow band at 1217 cm^{-1} observed for cellulose acetate samples is characteristic of a C-O-C bond vibration.

The PXRD analysis was also employed in characterisation of the cellulose acetate samples. It is used to determine the crystalline nature of materials. The NC's XRD pattern showed a diffractogram consistent with cellulose I.[11] The strong diffraction peaks of the characteristic cellulose crystal planes at 2θ values of 15.8º, 22.7º and 35. 8º observed in NC justified the typical cellulose crystalline form. The cellulose acetates diffractograms displayed loss of peaks to very weak peaks which is indicative of a low degree of crystallinity. This low degree of crystallinity compared with that of the original cellulose might be attributed to the substitution of the hydroxyl groups by acetyl groups. The data generated from the diffractograms showed that the amorphous region of the corn cob cellulose was increased to 70.7 and 77.6 for CA and CDA respectively upon acetylation. The peak at 2θ: 8.4 in CA

and CDA is associated with semi-crystalline acetylated cellulose derivatives. Other weak intensity peaks were detected at 2θ values of 10.7, 13.8, 19.5 and 23 and a maximum at 27°, indicating the presence of a semi-crystalline behaviour suggesting the cellulose triacetate structure. These peaks are caused by an increase in the inter-fibrillar distance induced by the presence of acetyl groups along with cellulose chains. This further explains the increased solubility as an increase in amorphous parts improves the solubility due to the increased free energy. The amorphous state of the cellulose acetate exhibits a disordered structure compared to its more crystalline state in the native cellulose hence enhanced solubility and this is in line with the SEM images that showed a disordered structure of the cellulose acetate and the native cellulose which had a compact structure.

4.5 Thermal Analysis

Differential scanning calorimetry was used to characterize the thermal property of the samples. The broad endothermic peak observed between 32.6 to 137.6 °C in native cellulose samples can be ascribed to the glass transition (Tg) and water desorption to a lesser extent. Similarly, Tg was also observed in CCA, CDA and CA around 48.9 to 144.7 °C, which indicates the transition from a rigid to a more flexible state of an amorphous material. The endothermic event agrees with the thermogravimetric curve (Figure. 5) of the cellulose samples measured, with weight loss observed within the temperatures of 150 to 220°C. The endothermic peak suggesting the melting process of the crystalline regions of CA and CDA is 208.2°C, and 230.2°C closely related to CCA 220.0°C. This is consistent with literature of a melting point of 230-300°C,[21] slight variations can be because of the difference in the degree of acetylation and molecular weight. The melting peak in the NC (312.3 °C) appears to be higher than CA, CDA and CCA. Although not always the case, a decrease in melting point could suggest improved solubility, hence the better solubility observed upon acetylation of the native cellulose. Degradation of cellulose acetate samples occurred at higher temperatures above the melting point, which was around 300-400°C, which is characteristic of thermal degradation of cellulose acetate.[22] The broad exothermic peak around 330°C can be attributed to the partial pyrolysis due to the fragmentation of carbonyl and carboxylic bonds from anhydrous glucose units giving carbon or monoxide carbon. The exothermic reaction during degradation might be associated with the dissociation of glycosidic bonds from the cellulosic chains and the degradation of the cycloglucose units.

The TGA thermogram (Figure 5) shows the thermal behaviour of the cellulose samples, NC had about 4.05% weight loss at around 150 °C while CA, CDA and CCA show 4.68, 5.19 and 3.60% weight loss, respectively around the temperature range of 150 to 200 °C. The weight loss in NC could be attributed to a dehydration reaction or impurities, while weight loss in CA, CDA and CCA could be attributed to the release of carbon dioxide, acetic acid, and other volatile compounds from the cellulose acetates. Further heating of the cellulose samples at higher temperatures shows a marked weight loss in the samples demonstrating the decomposition: For CA, a significant weight loss was observed at nearly 300 °C, which implies a degradation of the cellulose backbone of the polymer. This is characteristic of the thermal degradation of cellulose acetate. There was an increase in the thermal degradation temperature, which indicates increased thermal stability of the cellulose after acetylation,[23] and it is due to the replacement of OH groups with acetyl groups.

5. Conclusion

Cellulose extracted from corn cob residue was successfully acetylated under two different conditions to obtain two cellulose acetates with different degrees of substitutions (CA; 2.65 and CDA; 1.87). CDA showed characteristics of cellulose diacetate while CA showed characteristics of cellulose triacetate. The cellulose acetates had improved solubilities in some organic solvents and were amorphous in nature. Hence, low-cost corn cob-based cellulose acetate, which could be utilized as a polymer matrix for cellulose-based composite applications can be generated from corn cob residues.

CONFLICT OF INTEREST
No conflict of interest is associated with this work.

AUTHORS DECLARATION
The authors declare that this work was done by the authors named in this article and all liabilities pertaining to claims relating to the content of this article will be borne by them.

REFERENCES

1. Bhatt P, Trehan S, Inamdar N, Mourya VK, Misra A (2021) Polymers in drug delivery: an update. In: Applications of polymers in drug delivery. 2nd edn Elsevier.1-42. https://doi.org/10.1016/B978-0-12-819659-5.00001-X

2. Khoshnevisan K, Maleki H, Samadian H,

Shahsavari S, Sarrafzadeh MH, Larijani B, Dorkoosh FA, Haghpanah V, Khorramizadeh, MR (2018) Cellulose acetate electrospun nanofibers for drug delivery systems: Applications and recent advances. *Carbohydr Polym, 15 (198):131-141.*
https://doi.org/10.1016/j.carbpol.2018.06.072

3.   Seddiqi H, Oliaei E, Honarkar H, Jin J, Geonzon LC, Bacabac RG, Klein-Nulend J (2021). Cellulose and its derivatives: Towards biomedical applications. *Cellulose, 28(4): 1893-1931* https://doi.org/10.1007/s10570-020-03674-w

4.   Kupnik K, Primožič M, Kokol V, Leitgeb M (2020). Nanocellulose in drug delivery and antimicrobially active materials. *Polymers, 12(12):2825.*
https://doi.org/10.3390/polym12122825

5.   Han SO, Youk JH, Min KD, Kang YO, Park WH (2008). Electrospinning of cellulose acetate nanofibers using a mixed solvent of acetic acid/water: Effects of solvent composition on the fiber diameter. *Mater Lett, 62(4-5):759-762.*
https://doi.org/10.1016/j.matlet.2007.06.059

6.   Choi JY, Nam J, Yun BY, Kim YU, Kim S (2022). Utilization of corn cob, an essential agricultural residue difficult to disposal: Composite board manufactured improved thermal performance using microencapsulated PCM. *Ind Crops and Prod, 183(1), 114931*
https://doi.org/10.1016/j.indcrop.2022.114931

7.   Global Corn Market Analysis, 2019-2023: Production, Consumption, Exports, Imports and Yield [Internet]. https://www.globenewswire.com/news-release/2020/01/20/1972360/0/en/Global-Corn-Market-Analysis-2019-2023-Production-Consumption-Exports-Imports-and-Yield.html Accessed June 30, 2023

8.   Mohlala LM, Bodunrin MO, Awosusi AA, Daramola MO, Cele NP, Olubambi PA (2016). Beneficiation of corncob and sugarcane bagasse for energy generation and materials development in Nigeria and South Africa: A short overview. *Alexandria Engineering Journal, 55(3), 3025-3036.*
https://doi.org/10.1016/j.aej.2016.05.014

9.   Sarsaiya S, Jain A, Kumar Awasthi S, Duan Y, Kumar Awasthi M, Shi J (2019) Microbial dynamics for lignocellulosic waste bioconversion and its importance with modern circular economy, challenges and future perspectives. *Bioresour Technol. 291:121905*
https://doi.org/10.1016/j.biortech.2019.121905

10.   Azubuike CP, Okhamafe AO (2012) Physicochemical, spectroscopic and thermal properties of microcrystalline cellulose derived from corn cobs. *Int J Recycl Org Waste Agric.1(1):9.*
https://doi.org/10.1186/2251-7715-1-9

11.   Azubuike CP, Rodríguez H, Okhamafe AO, Rogers RD (2012) Physicochemical properties of maize cob cellulose powders reconstituted from ionic liquid solution. *Cellulose. 19(2):425–433.*
https://doi.org/10.1007/s10570-011-9631-y

12.   Shogren RL, Peterson SC, Evans KO, Kenar JA (2011) Preparation and characterization of cellulose gels from corn cobs. *Carbohydr Polym. 86(3):1351–1357.*
https://doi.org/10.1016/j.carbpol.2011.06.035

13.   Egot MP, Alguno AC (2018) Preparation and Characterization of Cellulose Acetate from Pineapple (Ananas comosus) Leaves. *Key Eng Mater. 772:8–12.*
https://doi.org/10.4028/www.scientific.net/KEM.772.8

14.   Akpabio U, Effiong I, Akpakpan A (2012) Preparation of Pulp and Cellulose Acetate from Nypa Palm Leaves. International Journal of Environment and Bioenergy 1(3): 179-194.

15.   Rodrigues Filho G, Monteiro DS, Meireles C da S, de Assunção RMN, Cerqueira DA, Barud HS, (2008). Synthesis and characterization of cellulose acetate produced from recycled newspaper. *Carbohydr Polym. 73(1):74–82.*
https://doi.org/10.1016/j.carbpol.2007.11.010

16.   Makadia J, Madu SJ, Arroo R, Seaton CC, Li M. (2022) Artemisinin–acetylenedicarboxylic acid cocrystal: screening, structure determination, and physicochemical property characterisation. *CrystEngComm. 24(5):1056–1067.*
https://doi.org/10.1039/D1CE01400E

17.   Homem NC, Amorim MTP (2020) Synthesis of cellulose acetate using as raw material textile wastes. *Mater Today Proc. 31:S315–S317.*
https://doi.org/10.1016/j.matpr.2020.01.494

18.   Azubuike C, Silva B, Okhamafe A. (2012) Pharmacopoeial and physicochemical properties of α-cellulose and microcrystalline cellulose powders derived from cornstalks. *Int J Green Pharm. 6(3):193.*
https://doi.org/10.4103/0973-8258.104930

19.   Jia X, Guo D, Yan Q, Yu H, Lyu Q, Han L, Zhou C, Xiao W (2022) Synthesis and Characterization of Corn Stover-Based Cellulose Triacetate Catalyzed by Ionic Liquid Phosphotungstate. *Int J Mol Sci. 17;23(12):6783.*
https://doi.org/10.3390/ijms23126783

20.   Das AM, Ali AA, Hazarika MP (2014) Synthesis and characterization of cellulose acetate from rice husk: Eco-friendly condition. *Carbohydr Polym. 112:342–349.*

https://doi.org/10.1016/j.carbpol.2014.06.006

21.   Wu S, Qin X, Li M (2014) The structure and properties of cellulose acetate materials: A comparative study on electrospun membranes and casted films. *J Ind Text. 44(1):85–98.* https://doi.org/10.1177/1528083713477443

22.   Lee J, Lee J, Jeon H, Park H, Oh S, Chung I. (2020) Studies on the melt viscosity and physico-chemical properties of cellulose acetate propionate composites with lactic acid blends. *Molecular Crystals and Liquid Crystals. 707(1):8-20* https://doi.org/10.1080/15421406.2020.1741814

23.   Wsoo MA, Shahir S, Bohari SP, Nayan NH, Abd Razak SI (2020) A review on the properties of electrospun cellulose acetate and its application in drug delivery systems: A new perspective. *Carbohydr Res. 491:107978.* https://doi.org/10.1016/j.carres.2020.107978