CELLULOSE CHEMISTRY AND TECHNOLOGY

EFFECTS OF BALL MILLING AND ENZYME TREATMENT ON CELLULOSE ACETYLATION

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A novel process was developed to produce cellulose acetate from bleached hardwood kraft pulp (BHKP) through ball milling and cellulase treatment. The ball milling and/or cellulase treatment of BHKP increased the esterification reaction, but enzyme treatment reduced the viscosity of the produced cellulose acetate (CA). The degree of substitution (DS) values upon acetylation were 2.26 for BHKP, 2.61 for ball-milled BHKP and 2.91 for ball milled followed by cellulase treatment of BHKP. The prepared CA was also characterized by FTIR, XRD, TGA, ^{1}H-NMR and SEM. A strong band for –OH stretching of cellulose disappeared and created a strong band for carbonyl (C=O) group on esterification of BHKP. The crystallinity index of BHKP was 63.3%, which completely disappeared on acetylation, demonstrating the successful esterification of cellulose. The initial weight loss of cellulose acetates was lower than that of the native cellulose, as observed in TGA, indicating the acetylated samples are less hydrophilic. ^{1}H NMR spectroscopy confirmed the complete structure of cellulose acetate.

Keywords: BHKP, cellulose acetate, acetylation, degree of substitution

INTRODUCTION

Cellulose acetate (CA) is a cellulose derivative with a wide range of properties, depending on its degree of substitution (DS).[1] Also, depending on its solubility in common solvents, molecular weight and melting properties, CA can be used in the manufacture of a variety of consumer products, including textiles, plastics, films, cigarette filters and others. CA is considered a biodegradable polymer within the scientific community.[2,3] Still, increased awareness of routes of degradation could prove useful to understand the ultimate environmental impact of CA based products.

Many studies were carried out on CA preparation from different non-woody materials, including wheat straw,[4] bagasse,[5,6] banana rachis,[7] coconut palm leaf/trunk[8] *etc*. Conventionally, CA is produced from native cellulose using acetic acid and acetic anhydride in the presence of sulfuric acid catalyst.[9] Nabili *et al.*[10] prepared cellulose triacetate (CTA) from microfibrillated date seed cellulose, using the conventional acetylation method with acetic anhydride as acetyl donor, acetic acid as solvent, and sulfuric acid as catalyst. In this process, cellulose was acetylated without dissolving the material throughout. Candido *et al.*[11] synthesized CA from sugarcane bagasse: firstly, cellulose was extracted from bagasse, and then it was acetylated. Cerqueira *et al.*[12] optimized sugarcane bagasse cellulose acetylation by varying acetic acid, acetic anhydride and catalyst volume, as well as reaction and activation times. Intrinsic viscosity was used as a parameter for determining the quality of the produced material. Fan *et al.*[13] isolated cellulose from rice straw by pretreatment with dilute alkaline and acid solutions successively, and then converted it into CA in the presence of acetic anhydride and phosphotungstic acid. Phosphotungstic acid ($H_3PW_{12}O_{40}$) was found to be an effective catalyst for the acetylation of the cellulose derived from rice straw. Biswas *et al.*[14] also prepared cellulose acetate from different agricultural residues, such as corn fiber, rice hulls and wheat straw. These studies carried out cellulose extraction from their respective raw materials prior to cellulose acetylation, but the methods used did not involve a chemical recovery system. From a commercial point of view, cellulose extraction (pulping) is capital intensive. The most common and established pulping method is the kraft process. Therefore, in this investigation, hardwood kraft bleached pulp (BHKP) is used as a starting raw material.

Several attempts have been made to improve the esterification of cellulose. Microwave irradiation proved to be a rapid, uniform and efficient method, allowing easy access into the particles for esterification.[15,16] Li *et al.*[16] prepared CA by a solvent-free acetylation of cellulose with acetic anhydride under microwave heating with iodine as a catalyst. The results showed that the DS increased as the amount of iodine increased. Ria *et al.*[17] showed that the refined pulp in a PFI mill increased methylation in methyl cellulose preparation. In another study, it was observed that refined cellulose pulp had higher surface area, consequently contributing to a higher DS value in carboxymethyl cellulose preparation.[18] Mondal *et al.*[19] prepared food grade CMC from corn husk with high DS. The solubility, molecular weight, and DS of the prepared CMC increased with decreasing cellulose particle sizes.

Enzymatic treatment facilitates the reactivity of cellulose.[20] Cellulase has been reported to improve the reactivity/accessibility of dissolving pulp, and xylanase – to increase the purity of the dissolving pulp.[21] Considering that the main constituent of BHKP is cellulose, cellulase enzyme was chosen in the present work for cellulose treatment. It is expected that this treatment would increase the accessibility of BHKP to subsequent acetylation. To the best of the authors' knowledge, no reports have been published so far on the mechanical and enzymatic treatments of cellulose preceding cellulose acetate preparation. Therefore, in this investigation, BHKP was ball milled to different particle sizes, and BHKP and ball milled BHKP were treated with cellulase to improve the subsequent esterification reaction of cellulose.

EXPERIMENTAL

Materials

Bleached hardwood kraft pulp (BHKP) was collected from Basundhara Paper Mills, Bangladesh. Acetic anhydride (98%), sodium hydroxide (98%) and ethanol (99.9%) were purchased from Merck (Germany), and glacial acetic acid (99.8%), hydrochloric acid (37%) and cellulose acetate were received from Sigma-Aldrich. The chemicals were used without further purification. Endoglucanase-rich cellulase (FiberCare U) was provided by Novozymes A/S (Denmark). The cellulolytic activity (determined as Na-CMC activity) was 219 u/mL.

Ball milling of pulp

BHKP was shredded by a juice mixer. Then, small pieces of dry pulp of 10 g were milled in a planetary ball mill (Fritsch GmbH, Pulverisette 5), with a 500 mL zirconium dioxide bowl and 80 zirconium dioxide balls (diameter of 1 cm). The milling frequency was 300 rpm for 2 h.

Particle size

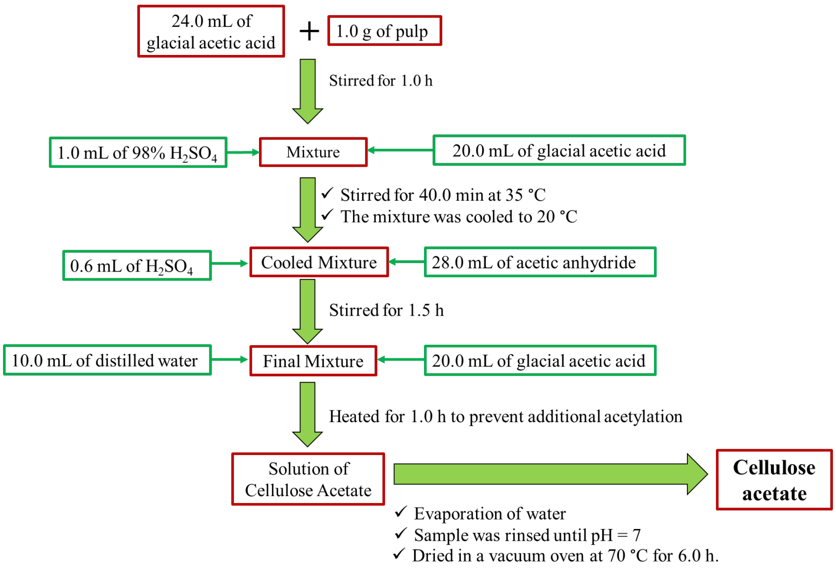
The ball-milled pulp sieving was carried out by a Fritsch Analysette 3 sieve system. Sieving was conducted using a mechanized sieve shaker and mesh sieves with known opening sizes. After testing was complete, the mass of the powder left in each sieve was weighed. The results were presented as mass % due to the fact that the samples taken for particle size distribution are representative. For the purpose of the study, 5 g of pulp with mesh sizes of M50, M100, M200, and M400 were obtained.

Enzyme treatment

For the modification of the surface of BHKP, enzymatic (cellulase) treatment was carried out according to the method reported in the literature[22] with a few modifications. The pulp (5 g) was added to 95 mL of sodium acetate buffer solution (pH 4.9) in a beaker. Then, 0.1 mL of cellulase enzyme was added to the mixture. The mixture was placed in a closed water bath for 2 h, while the water bath temperature was maintained at 40 °C.

Synthesis of cellulose acetate

The synthesis of CA was carried out following the method described previously, with a few modifications.[11] A schematic diagram for the preparation of cellulose acetate from pulp has been presented in Scheme 1. 24 mL of glacial acetic acid was added to 1 g of pulp. After stirring the mixture for 1 h, 20 mL of glacial acetic acid and 1 mL of 98% H_2SO_4 were added. The mixture was then stirred for an additional 45 minutes. Throughout the entire procedure, the temperature was maintained at 35 °C, and the process was carried out using a heating magnetic stirrer.



Scheme 1: A schematic diagram for the preparation of cellulose acetate

After that, the mixture was cooled to 20 °C, and 28 mL of acetic anhydride and 0.6 mL of H_2SO_4 were added. The mixture was thereafter stirred for 1.5 h. In the final step of the reaction, 20 mL of glacial acetic acid and 10 mL of distilled water were added, and the mixture was heated for 1 h to prevent additional acetylation. In the majority of instances, an obvious solution was observed. The mixture was then disposed of in water and rinsed with distilled water until the pH reached 7.0. After reaching the desired pH (~7.00), the product was dried in a vacuum oven at 70 °C for 6 h.

Determination of degree of substitution (DS)

A 0.1 g of sample was taken for the determination of the DS in a conical flask. 5 mL of ethanol and then 5 mL of 0.25 M NaOH were added to the sample. Then, the mixture was kept in the dark for 24 h covered with aluminum foil. In the subsequent stages, 0.25 M HCl was added to the mixture, which was then allowed to settle for 30 minutes to permit the completion of the HCl-NaOH reaction. Using phenolphthalein as an indicator, the mixture was titrated with NaOH solution. The %AG and DS were calculated according to the method in the literature:[23]

$$\%AG = \frac{\{[(Vbi + Vbt) \times Cb - (Va \times Ca)] \times M \times 100\}}{mac} \quad (1)$$

where Vbi – volume of NaOH added to the system (L), Vbt – volume of NaOH spent in titration (L), Cb – NaOH concentration (M), Va – volume of HCl added to the system (L), Ca – HCl concentration (M), M – molar weight of acetyl group (43 g mol^{-1}), mac – weight of cellulose acetate sample (g).

This % AG value leads to the calculation of the degree of substitution (DS) as follows:

$$DS = \frac{386 \times \%AG}{10240 - \%AG} \quad (2)$$

Yield measurement

The percent yield of the product was measured based on the dry weight basis and was calculated using the following equation as:[18]

$$Yield\ (\%) = \frac{Weight\ of\ dried\ CA}{Weight\ of\ dried\ cellulose} \times 100 \quad (3)$$

Molecular weight

1% of the prepared CA was dissolved in DMSO solution and the intrinsic viscosity was determined at 25 °C, using an Anton Paar Microviscometer (Model: Lovis 2000M). From the intrinsic viscosity, the molecular weight of the CA was calculated following the “Mark-Houwink-Sakurada” equation:[24]

$$[\eta] = K\,M^{a} \quad (4)$$

where K is a constant for the solvent, a is the polymer shape factor, $[\eta]$ is the intrinsic viscosity, and M is the molecular weight of CA. The molecular weight of the prepared CA was calculated according to the equation (4), using the value of K = 0.001710 dL/g and a = 0.610 at 25 °C.[25]

Dynamic viscosity measurement

Dynamic viscosity of the prepared CAs were measured by a rotational rheometer (Anton-Paar, Model: RheolabQC), using a measuring cup (C-DG26.7/SS.QC-LTD) and a cylinder (double gap, DG26.7) with a variable shear rate, 10-500 s^{-1} at 25-85 °C in 5 °C intervals.

Image analysis

A drop of diluted samples of initial pulp, refined pulp, enzyme treated pulp and CA was taken on a slide, and images were taken in a Euromex-Oxion image analyzer using Image Focus Alpha software. Scanning electron microscopy (SEM) images of untreated pulp, enzyme treated pulp and CA were also recorded (AG EV018, Carl Zeiss, Germany).

Thermogravimetric analysis (TGA)

The thermal properties of BHKP and synthesized CAs were investigated using a Hitachi TGA instrument (TG-DTA 6200), operated from 30 to 550 °C, at a heating rate of 10 °C min^{-1} under N_2 atmosphere (100 mL min^{-1}) in open aluminum pans.

X-ray diffraction (XRD) analysis

The crystallinity of the BHKP and synthesized CA was analyzed by an X-ray diffractometer (XRD) (ARL™ EQUINOX 1000, Thermo Fisher Scientific, USA). The instrument was operated at 40 kV and 15 mA, with CuK alpha radiation of 1.5606 angstrom wavelength, and the acquisition time was 10 minutes. The crystallinity index (*I*c) was calculated using the following formula:[26]

$$Ic = \frac{I_{002} - I_{am}}{I_{002}} X\ 100 \quad (5)$$

where I_{002} is the maximum intensity of diffraction of the (002) lattice peak at a 2θ angle of 22° and I_{am} is the intensity of diffraction of the amorphous material, which is taken at a 2θ angle of 18°.

FT-IR spectroscopic analysis

Attenuated total reflectance–Fourier transform infrared (ATR-FT-IR) spectroscopy was used to characterize the pulp and the synthesized CA samples. A FT-IR spectrophotometer (Frontier, Perkin-Elmer, UK; Software: Spectrum version 10.4.4) was used. The FT-IR spectra were collected in ATR mode, equipped with a diamond crystal. Before each measurement, a background scan was performed and acetone was used to clean the diamond crystal. The spectra were collected within the range from 650 to 4000 cm^{-1} at 4 cm^{-1} spectral resolution and with 12 scans per spectrum.

Measurements of ^{1}H NMR spectra

^{1}H-NMR measurement of the prepared sample CA4 was performed using a 400 MHz FT-NMR spectrometer (Model: 400™ ASCEND, Bruker, Switzerland). Deuterated chloroform ($CDCl_3$) was used as a solvent for ^{1}H-NMR analysis and tetramethylsilane (TMS) as an internal standard.

RESULTS AND DISCUSSION

The solubility and the mechanical, chemical, physical, and thermal properties of CA depend on its DS value. The DS value of the CA prepared from BHKP was 2.26, which increased to 2.61 upon ball milling of BHKP to a mesh size of 100. This happened due to the thus-achieved higher surface area, which increases the contact surface between reactants and cellulose particles, thus raising the reaction rate, and ultimately increases the DS values. The DS value was quite high as the starting raw material was free from lignin. The presence of lignin interferes directly with the product of the acetylation reaction. Rodrigues Filho *et al.*[27] observed that homogeneous acetylation of as-received newspaper was insufficient for 24 h of reaction, thus, the material was acetylated for 48 h and the DS value was 1.98 ± 0.02. However, the delignified newspaper dissolved in the solvent system at the beginning, and the DS value was 2.79 ± 0.02 for 24 h.

Surface modification of BHKP fiber was carried out by cellulase enzyme and the results of esterification are shown in Table 1. The DS value increased from 2.25 to 2.48 in the untreated pulp, which was lower than the DS value of ball-milled BHKP. In order to observe the synergistic effects on the acetylation of cellulose, ball milling followed by cellulase treatment was carried out. The DS value of ball milled and then cellulase treated fiber increased to 2.91. As shown further in SEM analysis, pulp fiber cracked on cellulase treatment, which facilitated diffusion of acetic anhydride into the inner OH groups available to the reaction. Li *et al.*[16] proposed that at the beginning, the reaction is heterogeneous, and OH groups on the surface of solid cellulose will be preferentially acetylated, then, as the acetylation progresses, the acetylated cellulose gradually dissolves in the reaction medium and the remaining unreacted hydroxyls become available. This happened in the case of ball milling, followed by cellulase treatment.

The yield of CA increased with the DS value. The CA yield from BHKP was 90.55% at the DS value of 2.26, while the CA yield from ball-milled and enzyme treated BHKP was 135.92% at the DS value of 2.91. The -OH groups were replaced by heavier acetate groups as the DS values increased. Similar results were observed for carboxymethylcellulose preparation.[18,19]

As shown in Table 1, the highest and the lowest intrinsic viscosity and molecular weights observed for the prepared CA from BHKP were of 34.36 and 6025, and for CA from ball-milled and enzyme treated BHKP – of 19.72 and 2398, respectively. This can be explained by the enzymatic degradation of cellulose.

Table 1
Solubility, degree of substitution (DS), intrinsic viscosity, and molecular weight (MW) of CA synthesized from hardwood bleached pulp (HWBP) (CA1), 100 mesh pulp (CA2), enzyme-treated raw pulp (CA3), and enzyme-treated 100 mesh pulp (CA4)

Sample name	Solubility in DMSO	Solubility in acetone	DS	Intrinsic viscosity (mL/g)	Molecular weight
CA1	Highly soluble	Insoluble	2.26 ± 0.205	34.36 ± 1.43	6025 ± 195
CA2	Highly soluble	Insoluble	2.61 ± 0.211	21.86 ± 1.05	2884 ± 59
CA3	Highly soluble	Insoluble	2.48 ± 0.210	32.31± 1.25	5495 ± 189
CA4	Highly soluble	Insoluble	2.91 ± 0.212	19.72± 0.95	2398 ± 61

ATR-FTIR analysis of the prepared CAs

The strong band at 3334 cm^{-1} in cellulose is due to –OH stretching, which completely disappeared in the spectra of cellulose acetates. A strong band of the carbonyl (C=O) group at 1738 cm^{-1} in all prepared cellulose acetates was observed, which confirmed the successful chemical conversion to an ester. The disappearance of –OH stretching and creation of a strong band of carbonyl (C=O) group were also observed by Shaikh *et al.*[8] Rodrigues Filho *et al.*[27] also showed the presence of a strong intensity band at 1746 cm^{-1} assigned to the stretching of the carbonyl group of cellulose acetate, and a consequent reduction in the intensity of the band for OH stretching in 3460 cm^{-1}. The bands at approximately 1050 cm^{-1} for C–O–C in the anhydroglucose units of cellulose were also clearly seen. As seen in Figure 1, the intensity of this band was almost similar, which indicated that the esterification occurred only in –OH groups.[8] The bands at 1341 cm^{-1} and 1220 cm^{-1}, corresponding to C–H bending and C–O stretching vibrations of the acetyl group, respectively, were also observed. Das *et al.*[28] also observed increased band intensity for the carbon-hydrogen (C-H) bending vibration at 1369 cm^{-1} and carbon-oxygen (C-O) stretching vibration at 1220 cm^{-1}. The intensity of the band (896 cm^{-1}) of the amorphous region in cellulose acetate was higher than that in the BHKP.

X-ray diffraction analysis of the prepared CAs

Figure 2 presents the XRD patterns of BHKP and cellulose acetates obtained by different methods. The main peak for BHKP was observed at 22.7° 2θ, attributed to crystalline cellulose, which corresponds to the (200) plane.[29,30] An intense peak at approximately 15.6° 2θ corresponds to the overlapped peaks of the crystallographic planes with Miller indices (1_10) and (110). These peaks completely disappeared in the XRD patterns of CA, demonstrating the successful esterification of cellulose. The crystallinity index of BHKP was 63.3% (Table 2), which completely changed on acetylation. Other studies also showed the disappearance of these peaks on esterification.[31] The inter- and intramolecular hydrogen bonds of cellulose were almost completely broken during the substitution of hydroxyl groups by acetyl groups. Low intensity diffraction peaks of semi-crystalline CAs appeared at 8.3°, 10.4° and 13.3° 2θ, while the diffraction peak for the amorphous material is found at 17.5° 2θ.[32] Chen *et al.*[33] also observed similar XRD patterns for CA.

Thermogravimetric analysis of the prepared CAs

The thermal analysis of the prepared CAs was carried out to determine the thermal stability of the products. The TGA curves of BHKP and prepared CAs are illustrated in Figure 3.

Table 2
Thermal degradation temperature and crystallinity of different cellulose acetates and HWBP

Sample name	Onset decomposition temperature, T_d (°C)	Crystallinity (%)
CA1	310	
CA2	318	
CA3	297	
CA4	319	
HWBP	346	63.3

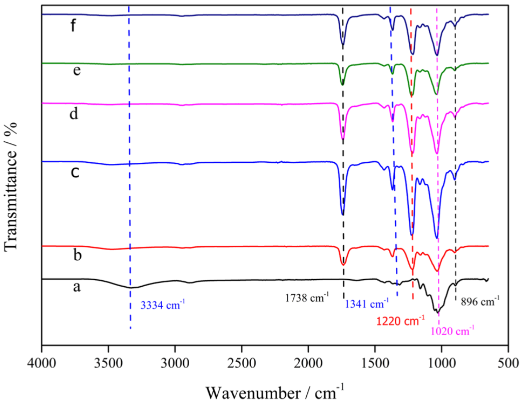


Figure 1: ATR-FTIR spectra of (a) BHKP, (b) standard CA, (c) CA synthesized from raw pulp (CA1), (d) CA synthesized from 100 mesh pulp (CA2), (e) CA synthesized from enzyme treated BHKP (CA3), and (f) CA synthesized from enzyme treated 100 mesh pulp (CA4)

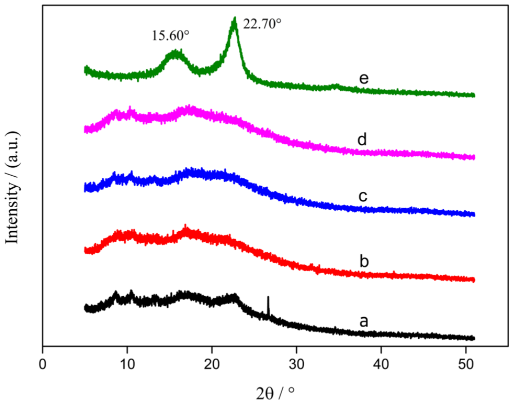


Figure 2: XRD patterns of (a) CA synthesized from raw pulp (CA1), (b) CA synthesized from 100 mesh pulp (CA2), (c) CA synthesized from enzyme treated raw pulp (CA3), (d) CA synthesized from enzyme treated 100 mesh pulp (CA4) and (e) hardwood bleached pulp (HWBP)

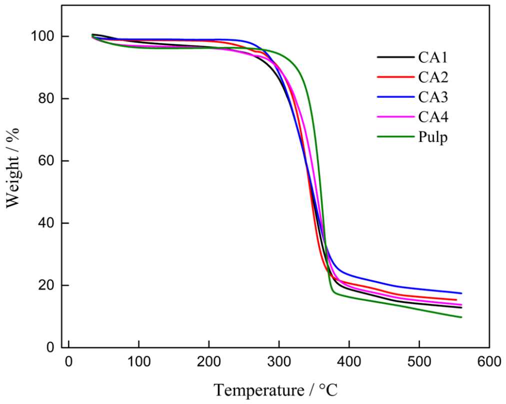


Figure 3: TGA curves of different cellulose acetates and hardwood bleached pulp

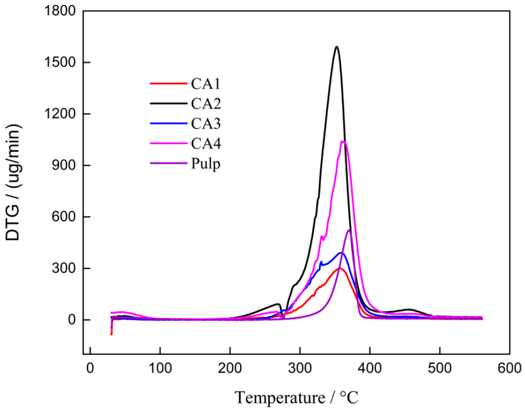


Figure 4: DTG curves of different cellulose acetates and hardwood bleached pulp

All these samples showed three main thermal events, which are commonly observed for cellulose derivatives.[18] At 100 °C, BHKP lost about 4 wt%, while the CAs lost only 2 wt%, which was caused by the desorption of water. The lower weight loss of acetylated cellulose samples indicated that the acetylated samples are more hydrophobic than the native cellulose. Similarly, other studies showed that acetylated products are more hydrophobic than native cellulose.[28] Then, weight remains almost constant up to 285 °C for BHKP and up to 214 °C for CAs. After this level, degradation suddenly started at 287 °C and continued up to 378 °C for BHKP, while for CAs it started at 240-250 °C and continued up to 370-375 °C. As shown in the DTG graph in Figure 4, the maximum weight loss rate peaks were observed at 370 °C for BHKP, 360 °C for CA1, 353 °C for CA2, 360 °C for CA3 and 364 °C for CA4. These results comply with previous research on cellulose triacetate.[8] Barud *et al.*[34] reported that the thermal stability of cellulose ester increases with an increment in DS and molecular weight. Near this temperature range, cellulose undergoes dehydration, depolymerization, and the decomposition of glycosidic units, resulting in the formation of carbon residue.[10] At the temperature of 377 °C, the weight loss was 82% for BHKP, 80% for CA1, 78% for CA2, 73% for CA3 and 76% for CA4. From this temperature to 560 °C, the decomposition rate decreased sharply depending on the uniformity of the esterification, and generated 19 wt% char for BHKP and 13-18 wt% char for CAs.

SEM analysis

The morphology of the starting materials and CA is presented by SEM images in Figure 5. Cracking on the fiber surface was observed in enzyme-treated fibers (Fig. 5c), while a little difference was found in BHKP and ball-milled BHKP. Also, some debris on the fiber surface were seen on ball milled BHKP. As shown in Figure 5d, CA fibers were characterized by a porous structure. The DS value of CA synthesized from enzyme-treated 100 mesh size pulp was 2.91, indicating the acetylation reaction occurred simultaneously on the surface of fibers and within them, which causes honeycomb-like holes of the entire particle. Cao *et al.*[35] showed that CA with DS 2.84 was rich in small holes and almost all the cellulose structure was destroyed.

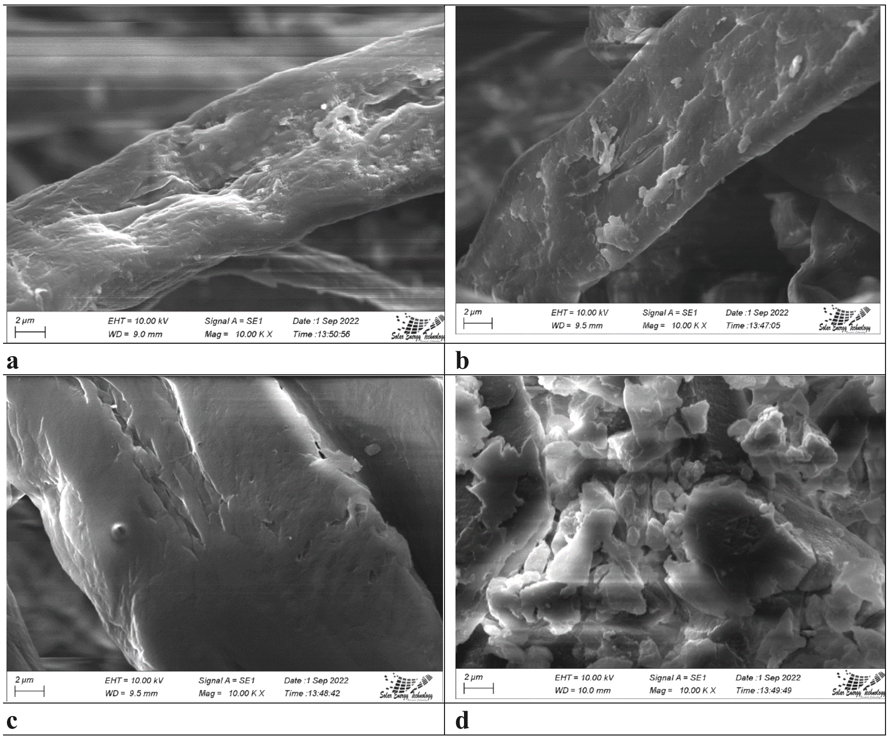


Figure 5: SEM micrographs of (a) raw pulp, (b) 100 mesh pulp, (c) enzyme treated 100 mesh pulp, and (d) cellulose acetate synthesized from enzyme treated 100 mesh pulp

Viscosity of CA solution in DMSO

The viscosity of 1% CA solution in DMSO was evaluated under different temperatures from 25 to 85 °C, and as expected, the viscosity of all CA solutions decreased with increasing temperature (Fig. 6). The heating provides the required energy for the movement of CA polymer chains by overcoming the intermolecular forces, and decrease in the viscosity.[33] CA prepared from BHKP showed the highest viscosity and CA prepared from enzyme treated 100 mesh BHKP showed the lowest viscosity at any temperature. This result is consistent with the intrinsic viscosity and molecular weight data in Table 1. Chen *et al.*[33] showed that the viscosity of the CA solutions depends on the types of raw materials used. A high DP cellulose material produces long molecular chains of CA, which are easily entangled under external forces, resulting in high viscosity.

^{1}H NMR analysis of cellulose acetate

Figure 7 shows the ^{1}H-NMR spectrum of prepared cellulose acetate having the DS of 2.91. As usual, the hydrogen atoms in methyl ($-CH_3$) groups of acetyl groups were detected at approximately 2.1 ppm. The signal at 1.9 ppm corresponds to hydrogen connected to the third carbon atom (C3) in the cellulose skeleton, while the signal at 2.1 ppm corresponds to the hydrogen of the sixth carbon atom (C6). The peaks in the region of 5.20-2.80 ppm correspond to the seven-ring protons of anhydroglucose (AGU). The signals at 4.4, 4.8, 5.1, 3.7, 3.5 and 4.3 ppm correspond to the C1, C2, C3, C4 and C5 atoms, respectively, and the signal at 4.0 ppm – to C6 and C6₀ of AGU.[36] The integration of ^{1}H-NMR spectrum was used for calculating the DS.[37] The ratio of 1/3 of the acetyl area to 1/7 of the anhydroglucose area was given the DS value of 2.96, which was close to the conventional method (2.91).

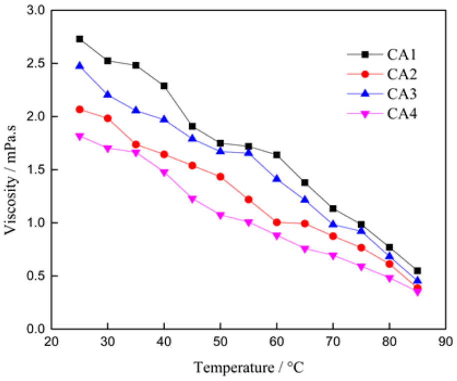


Figure 6: Viscosity plots of 1 wt% CA solution samples in DMSO as a function of temperature

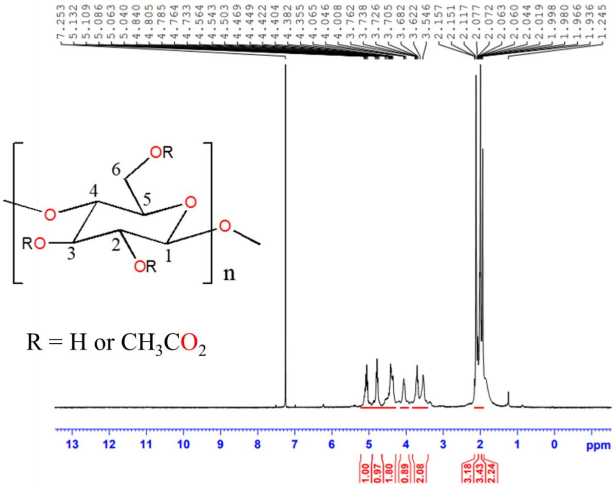


Figure 7: ^{1}H NMR spectrum of cellulose acetate synthesized from enzyme treated 100 mesh pulp (CA4)

CONCLUSION

The present investigation showed that the cellulose acetate could be produced from BHKP by ball milling, followed by enzyme treatment, while viscosity was decreased. The XRD pattern indicated the crystalline nature of BHKP diminished on acetylation. The thermal analysis showed a good thermal stability of the prepared triacetate. FTIR spectroscopy and ^{1}H NMR spectroscopy allowed the complete structural elucidation of cellulose acetate. Thus, the overall results suggest that the prepared cellulose acetate can be utilized as a polymer matrix for biodegradable cellulose-based composites for a variety of applications.

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