THE CHEMICAL AND SPECTRAL ANALYSES OF THE PREPARED CELLULOSE ACETATES FROM WHEAT STRAW POWDER AND SAWDUST POWDER

Yi Yi Lwin[1], Thida Kyaw[2], Yi Yi Myint[3]

Abstract

In this research, the preparation of cellulose powders from the wheat straw powder and sawdust powder by dewaxing and pulping processes, the preparation of cellulose acetates by the sonification process, and the identification of prepared cellulose acetates by chemical and spectral analyses were carried out. The cellulose acetates were prepared by the optimized acetylation of respective celluloses with an acetic acid-acetic anhydride-toluene solvent mixture using perchloric acid as a catalyst increasing the reaction rate for 1, 2, 3, and 4 h of sonication. The acetylation procedure was modulated by an ultrasonic cleaner. Then, the prepared cellulose acetates (WSCAs and SDCAs) from wheat straw powder and sawdust powder had been identified by chemical (acid-base titration) and spectral (FT IR, XRD, NMR) analyses for the degree of substitution of acetyl groups on the corresponding prepared cellulose acetates. From the titration data, FTIR spectral data and XRD spectral data, the optimum acetylation by 1 h sonication, which provides the highest degree of substitution and the highest yield percent, had been selected. Then WSCA-1 and SDCA-1 obtained by selected acetylation were further identified by ^{1}H and ^{13}C NMR (Nuclear Magnetic Resonance) spectroscopic methods.

Keywords: acetylation, sonication processes**,** acid-base titration, FT IR, XRD, NMR

Introduction

Cellulose acetate is a well-known industrial product that finds many commercial applications (Edgar *et al.*, 2001). It is used as a film base in photography, as a component in some coatings, and as a frame material for eyeglasses, as a synthetic fiber in the manufacture of cigarette filters and playing cards, as a fiber in textiles because of its relatively low cost, draping quality, softness, comfort, luster, and natural feel, as a substrate for motion picture camera film, as an ingredient in sheet and molded objects **(**Morgan, 2013). Cellulose acetate is typically made from wood pulp (cellulose) through reaction with acetic acid and acetic anhydride in the presence of sulphuric acid as a catalyst. Cellulose triacetate, (triacetate, CTA or TAC) is significantly more heat resistant than cellulose diacetate (Lindsey, 2010). In recent years, there has been strong emphasized to develop new cellulose-based materials because of the biodegradability and renewable aspects of these materials. Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to many thousands of β (1-4) linked D-glucose units. Cellulose can be produced from sources of lignocellulosic materials such as corn stalks, wheat straw, rice straw, agricultural by products such as corn fiber, rice hulls etc. **(**Crawford,1981; Updegraff, 1969).

The aim of this research is to prepare cellulose acetates by time-limit sonication processes, and then analyze the prepared cellulose acetates by chemical (acid-base titration) method, spectral (FT IR, XRD, ^{1}H and ^{13}C NMR) analyses for the determination of the degree of substitutions, crystallinity indices and average crystallite sizes. The cellulose acetates have been used to fabricate the cellulose acetate membranes which would be applied in clinical sense such as the separation of hemoglobin variants by electrophoresis and in wastewater treatment such as removal of toxic materials (Yi Yi Lwin, 2020).

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NMR characterization of cellulose acetate and chemical shift assignments

Hiroyuki, Hisaho, and Shimizu (2015) investigated the cellulose acetates (CA) with degrees of substitution (DS) ranging from 2.90 to 0.92 by two-dimensional NMR spectroscopy. From the NMR spectroscopic analysis, the ^{1}H and ^{13}C NMR chemical shifts of the eight anhydroglucose units (AGUs) that contain CA are: 2,3,6-tri-, 2,3-di-, 2,6-di-, 3,6-di, 2-mono-, 3-mono-, 6-mono-, and unacetylated AGUs.

Materials and Methods

Sample Collection and Sample Preparation (Sampling)

The agricultural byproducts such as wheat straw and sawdust were collected from Myingyan Township, Myingyan District, Mandalay Region.

Wheat straw and sawdust raw materials were cut into small pieces, rinsed with water, and dried. The dried pieces were blended and sieved with a 120-mm mesh. After that, the powder dusts were sieved again with a 150-mm mesh. Then the sampling powders were collected to be used for cellulose isolation.

Preparation of Celluloses

In the preparation of cellulose, the powders were firstly dewaxed (removing pectin) by toluene-ethanol (2:1, v/v) and then pulping process was made by alkaline hydrolysis of dewaxed powders for 9 h refluxing with 15 % NaOH (removing lignin), and by bleaching (removing non-cellulosic coloring materials) (Yi Yi Lwin *et al.*,2020). The yield percent of prepared wheat straw and sawdust celluloses were calculated.

Preparation of Cellulose Acetate

Wheat straw and sawdust cellulose acetates were prepared by acetylation of the respective celluloses conducted with acetic acid- acetic anhydride-toluene solvent mixture in the presence of perchloric acid as a catalyst for 1, 2, 3 and 4 h sonication using ultrasonic cleaner.

Acetylation of wheat straw and sawdust celluloses by 1, 2, 3 and 4 h sonication

5 mL glacial acetic acid, 0.5 mL perchloric acid, and 10 mL of toluene were mixed and allowed to stand for 30 min. Then 1g of wheat straw cellulose was added and shaken thoroughly for 10 min. Then, 5 mL of acetic anhydride was added and shaken again for 30 min. In addition, 15 mL of acetic acid was added and the suspended solution was incubated in an ultrasonic cleaner under operating temperature of 80◦C for 1 h. Then the suspension was poured into the beaker containing 150 mL distilled water. Finally, cellulose acetate suspension was centrifuged, dried and weighed. The same procedure was performed under the operating temperature of 80°C for 2, 3 and 4 h sonication.

The above same procedures were also performed with the sawdust cellulose. The resultant cellulose acetates are shown in Figures 1 and 2. The yield percent of wheat straw cellulose acetates (WSCA-1, 2, 3 and 4) and sawdust cellulose acetates (SDCA-1, 2, 3 and 4) were calculated.

(a) (b) (c) (d) (e)

Figure 1. (a) Prepared WSC (b) WSCA-1, (c) WSCA-2, (d) WSCA-3 (e)WSCA-4

(a) (b) (c) (d) (e)

Figure 2. (a) Prepared SDC (b) SDCA-1, (c) SDCA-2, (d) SDCA-3, (e) SDCA-4

Determination of Degree of Substitution of Acetyl Groups in Prepared Cellulose Acetates

Acid-base titration

The degree of substitution (DS) is the average value of acetyl groups which replace the hydroxyl groups in the AGU units. The titrations were performed for the determination of DS. A 5.00 mL of NaOH (0.25 M) and 5 mL of ethanol were added to about 0.1 g cellulose acetate. Then, this mixture was left to stand for 24 h. After that, 10.00 mL of HCl (0.25 M) was added to the system. Next, the mixture was titrated with a standard (0.25 M) NaOH solution, using phenolphthalein indicator. This procedure was repeated in triplicate. The following equation was used to determine the percentage of acetyl groups (Kelly *et al*., 1989).

$$\text{Acetyl Group (\%)} = \frac{([(Vb_i + Vb_t)\mu_b - (V_a)\,\mu_a]\,43)}{m_{CA}} \times 100$$

(%) = percentage of acetyl groups
Vb_i = volume of NaOH added to the system
Vb_t = volume of NaOH spent in the titration
μ_b = concentration of NaOH
V_a = volume of HCl added to the system
μ_a = concentration of HCl
43 = molar weight of acetyl group
m_{CA} = weight of cellulose acetate sample

$$\text{Degree of substitution (D.S)} = \frac{[162\ \text{AG (\%)}]}{[43 \times 100 - 42\ \text{AG (\%)}]}$$

162 = the molecular weight of anhydroglucose unit (Badejo *et al.*, 2018)

FT IR spectroscopic analysis

The functional groups of prepared cellulose and cellulose acetates were identified by FTIR spectrometer and measured at the Department of Chemistry, University of Mandalay. From these spectral data, the degree of substitutions (DS) of acetyl groups in the prepared cellulose acetates were determined by the ratio of the peak area of carbonyl peak and that of hydroxyl peak (Cheng, *et al*., 2010).

Degree of Substitutions (DS) = $A_{C=O} / A_{OH}$

$A_{C=O}$ = peak area of carbonyl groups in ester, A_{OH} = peak area of OH groups

Determination of Crystallinity Indices and Average Crystallite Sizes of Prepared Cellulose Acetates by XRD (X-ray diffraction)

The prepared cellulose acetates were identified by XRD and measured at URC, University of Yangon. From the resulting XRD data, the average crystallite sizes and crystallinity indices and the crystallite sizes (D_{hkl}) for all cellulose acetates could be calculated according to the following relations (Regiani *et al.,* 1999).

$I_{CA} = 1 - I_{min} / I_{max}$

I_{CA} = the crystallinity index of CA

I_{min} = the intensity minimum between ° of 2θ

Debye Scherrer equation

$D_{hkl} = k\lambda / \beta_{hkl} \cos\theta$

hkl = the average dimension of the crystallites, (lattice planes)

D_{hkl} = the size of the crystallite

k = the Scherrer constant (0.84 or 0.9)

λ = the wavelength of the x-ray diffraction (0.154056 nm)

θ = the Bragg angle (reflection angle) for the crystal planes (hkl) (He, *et al.*, 2008)

Isolation of Pure WSCA and SDCA compounds from prepared crude WSCA-1 and SDCA-1 by Column Chromatography

The selected wheat straw and sawdust cellulose acetates **(WSCA-1 and SDCA-1)** obtained by acetylation with 1 h sonication had been purified by isolation with column chromatography for further investigation. (Figure 3) The results are shown in Table 1.

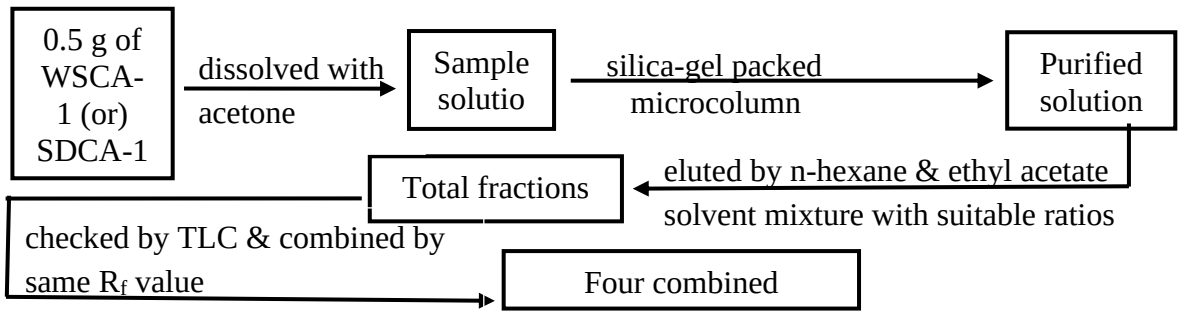


Figure 3. Flow diagram for isolation of pure WSCA and SDCA compounds from prepared crude cellulose acetates by column chromatography

Table 1. Combination of Fractions with Same R_f Values Checked by TLC (Thin Layer Chromatographic) Plates

Sample	Combining fractions	R_f values	Fraction with same R_f values	Sample	Combining fractions	R_f values	Fraction with same R_f values
WSCA-1	2 to 10	0.86	I	SDCA-1	3 to 8	0.86	I
	11 to 14	0.82	II		10 to 16	0.82	II
	17 to 29	0.62	III		19 to 27	0.62	III
	33 to 47	0.55	IV		30 to 38	0.55	IV

The resultant fractions of pure WSCA-1 and SDCA-1 compounds were analyzed by NMR spectroscopy at the Department Centre of Ningxia Organic Synthesis and Engineering Technology, Institute of Ningxia Academy of Agriculture and Forestry Sciences, Yinchuan, Ningxia, China. The resultant NMR spectra had been assigned and characterized by ^{1}H and ^{13}C NMR to determine the degree of substitution of acetyl groups on the prepared wheat straw and sawdust cellulose acetates.

Results and Discussions

Preparation of Cellulose

The celluloses were prepared from wheat straw and sawdust powders by dewaxing process with (2:1 v/v) toluene/ethanol mixture and by pulping process for 9-h refluxing with 15% NaOH. The yield percentages of dewaxed powder and cellulose in each process are shown in Tables 2 and 3.

Table 2. Yield (%) of Dewaxed Wheat Straw and Sawdust Powders by Extraction with (2:1 v/v) Toluene/Ethanol Mixture

No.	Type of sample powder	Weight of powder (g) (Before dewaxing)	Weight of powder (g) (After dewaxing)	Yield (%) of Dewaxed powder	Yield (%) of Pectin
1.	Wheat straw	100.00	96.04	**96.04**	**3.96**
2.	Sawdust	100.00	98.36	**98.36**	**1.64**

From the results of dewaxing process after removal of pectin, there is a higher composition of pectin (3.96%) in wheat straw powder which is one of the main constituents of plant than that (1.64%) in sawdust powder.

Table 3. Yield (%) of Wheat Straw and Sawdust Celluloses after Refluxing with 15% NaOH

No.	Type of sample powder	Weight of powder (g) (Before refluxing)	Weight of powder (g) (After refluxing)	Yield (%) of cellulose
1.	Wheat straw	10.00	3.43	**34.30**
2.	Sawdust	10.00	5.87	**58.70**

After removal of lignin**,** the wheat straw powder was found to contain 34.30 % cellulose and sawdust powder contained 58.70 % cellulose.

Preparation of Cellulose Acetate

Cellulose acetates were prepared by acetylation with various time limit sonication processes. The results are shown in Table 4.

Table 4. Yield (%) of (WSCA-1, -2, -3 & -4) and (SDCA-1, -2, -3 & -4) by Acetylation with 1, 2, 3 & 4 h Sonication Processes

No.	Types of CA	Weight of Cellulose (g) (before acetylation)	Weight of Cellulose Acetate (g) (after acetylation)	Yield (%) of cellulose acetate
1.	WSCA-1	1.0000	0.5324	**53.24**
2.	WSCA-2	1.0000	0.4948	49.48
3.	WSCA-3	1.0000	0.4865	48.65
4.	WSCA-4	1.0000	0.4588	45.88
1.	SDCA-1	1.0000	0.5761	**57.61**
2.	SDCA-2	1.0000	0.5527	55.27
3.	SDCA-3	1.0000	0.5443	54.43
4.	SDCA-4	1.0000	0.5298	52.98

The yield percents of 53.24% of WSCA-1 and 57.61% of SDCA-1 were obtained under the optimum condition (acetylation with acetic acid-acetic anhydride-toluene by 1-h sonication which gives the highest yield percent and higher degree of acetylation). Then, pure cellulose acetate compounds were separated by column chromatography. The fractions of pure WSCA-1 and SDCA-1 compounds had been isolated by n-hexane-ethyl acetate solvent system and were analyzed by ^{1}H and ^{13}C NMR spectroscopy.

Degree of Substitution of WSCA-1, -2, -3 &-4 and SDCA-1, -2, -3 & -4 by Acid-Base Titration

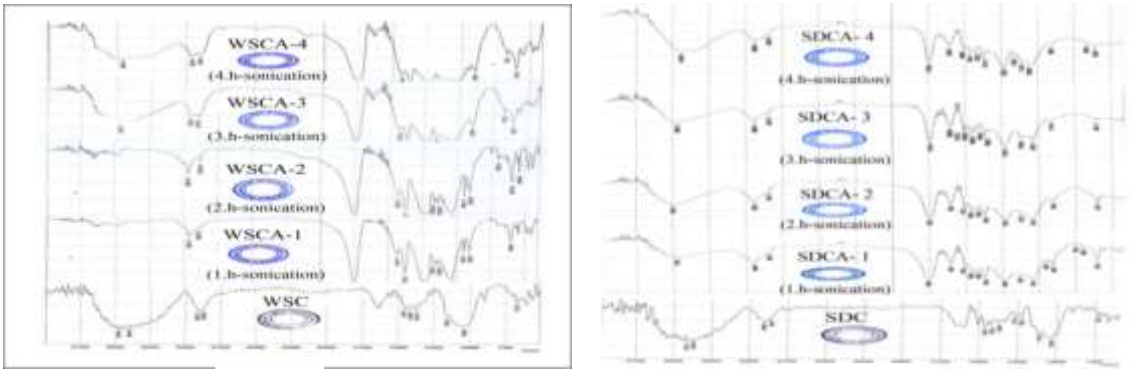
The prepared WSCAs and SDCAs were identified by the degree of substitution of acetyl groups in the prepared cellulose acetates. The results are shown in Table 5.

Table 5. Degree of Substitution of WSCA-1, -2, -3 & -4 and SDCA-1, -2, -3 & -4 by Acid-Base Titration

Types of CA sample	Weight of sample (mg)	Vol. of NaOH added, V_i(mL)	Vol. of NaOH Spent, V_t(mL)	Conc. of NaOH (μ_b)(M)	Vol. of HCl added (V_a)(mL)	Conc. of HCl (μ_a)(M)	AG (%)	Degree of substitution
WSCA-1	100.00	5.00	9.20	0.25	10.00	0.25	44.15	**3.04**
WSCA-2	100.00	5.00	8.80	0.25	10.00	0.25	40.85	2.56
WSCA-3	100.00	5.00	8.60	0.25	10.00	0.25	38.70	2.34
WSCA-4	100.00	5.00	8.40	0.25	10.00	0.25	36.55	2.14
SDCA-1	100.00	5.00	9.00	0.25	10.00	0.25	36.55	**2.79**
SDCA-2	100.00	5.00	7.90	0.25	10.00	0.25	26.90	1.69
SDCA-3	100.00	5.00	7.60	0.25	10.00	0.25	27.95	1.76
SDCA-4	100.00	5.00	7.20	0.25	10.00	0.25	23.65	1.45

From the results of titration, three acetyl groups substituted in anhydroglucose unit (AGU) of WSCA-1(3.04) and SDCA-1(2.79) compounds were calculated. So, these compounds could be expected to be **triacetate** and the other acetates could be assumed to be diacetates.

Degree of substitution of WSCA-1, -2, -3 & -4 and SDCA-1, -2, -3 & -4 by FTIR Spectroscopy



(a) **(b)**

Figures 4 (a) FTIR spectra of WSC and WSCA-1, 2, 3 & 4

(b) FTIR spectra of SDC and SDCA-1, 2, 3 & 4

According to the above Figures 4(a) and (b), there are no OH- stretching bands in WSCA-1. But all SDCA spectra show OH- stretching bands. The intensity of OH- stretching band were decreased gradually in the order of SDCA-1 > SDCA-2 > SDCA-3 > SDCA-4. So, acetylation with 1 h sonication seems to occur complete acetylation. Hence, the optimum time-limit is 1 h sonication. From these FTIR spectra, the peak areas of OH-peaks and the peak areas of C=O peaks had been calculated and the degree of substitutions of corresponding CAs had been calculated based on the values of peak areas according to Kelly., *et al* (1989).

Table 6. The Degree of Substitutions of Prepared WSCA-1, 2, 3 & 4 and SDCA-1, 2, 3 & 4 by 1, 2, 3 & 4 h Sonication Processes

No.	Types of sample	$A_{C=O}$	A_{OH}	Degree of Substitution	No.	Types of sample	$A_{C=O}$	A_{OH}	Degree of Substitution
1.	WSCA-1	14400	4800	**3.00**	1.	SDCA-1	16700	5600	**2.98**
2.	WSCA-2	14250	4875	2.92	2.	SDCA-2	19000	9800	1.94
3.	WSCA-3	17500	9625	1.82	3.	SDCA-3	22000	13700	1.61
4.	WSCA-4	15000	9000	1.67	4.	SDCA-4	17100	11250	1.52

$A_{C=O}$ = peak area of carbonyl groups in ester, A_{OH} = peak area of OH groups

According to Table 6, the degree of substitution, 3.00 indicates that WSCA-1 would be triacetate and those of the others indicate that WSCA-2, -3, -4 were assumed to be diacetates. Then, the degree of substitution, 2.98 indicates that SDCA-1 would be triacetate and those of the others indicate that SDCA-2, -3, -4 were assumed to be diacetates.

Crystallinity Indices and Average Crystallite Sizes of Prepared WSC & WSCA-1.2, 3, &4, and SDC & SDCA-1, 2, 3& 4 by XRD

The following XRD diffractograms show the isolated WSC, SDC by alkaline hydrolysis (refluxed with % NaOH for 9-hours), (WSCA-1, 2, 3 & 4) and (SDCA-1, 2, 3 & 4) acetylated by 1, 2, 3 & 4 h sonication (Figures 5 and 6)**.**

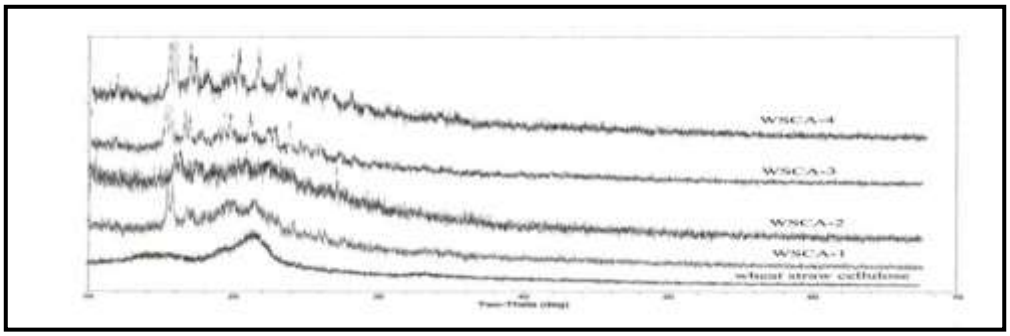


Figure 5. X-ray diffractograms of WSC and WSCA -1, 2, 3, and 4

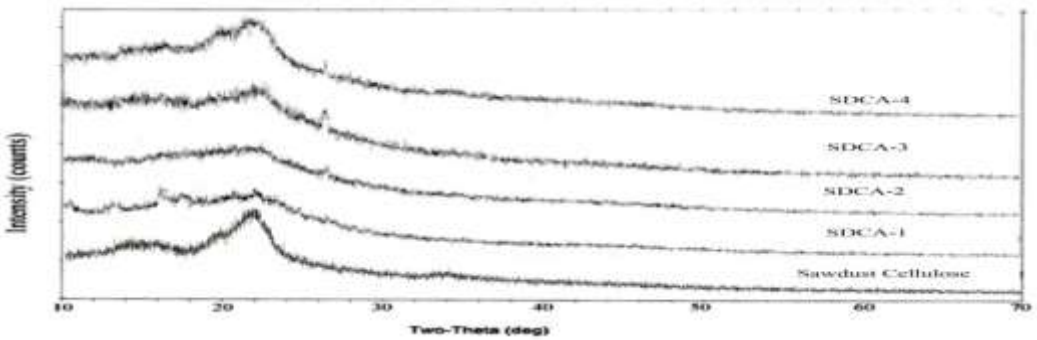


Figure 6. X-ray diffractograms of SDC, SDCA-1, 2, 3, and 4

In X-ray diffractogram of WSC, a sharp diffraction peaks at 17°.18°, 20°, and 21°(2θ) in WSC and SDC indicate the presence of cellulose. Diffractogram shows lower peak intensities at 20°(2θ) in WSCA-1, 2, 3 & 4 and at 17°, 18° (2θ) in SDCA-1, 2, 3 & 4 whereas sharp peaks at 17°, 18° (2θ) and broader peaks at 20°(2θ) in WSCA-1, 2, 3 & 4 and lower and broader peak intensities at 17°, 18° (2θ) in SDCA-1, 2, 3 & 4. The sharp peaks observed are due to their crystalline nature. The lower peak intensities indicate that the complete removal of non-cellulose due to alkaline hydrolysis and acetylation occur (Bledzki *et al.*, 1999). The crystallinity index of WSC and SDC was only one value, 0.65. The crystallinity indices decrease gradually from WSCA-1, 2, 3, & 4 and SDCA-1, 2, 3, & 4 but the particle sizes increase, in WSCA-1.2.3 & 4 and in SDCA-1, 2, 3, & 4 which were calculated by Debye Scherrer equation from the data of diffraction peaks (Table 7). The higher crystallinity indices indicate the greater elimination of both lignin and hemicelluloses which are amorphous substances (Fu and Lucia, 2003). So, it could be assumed that pure WSCA-1 and SDCA-1 were assumed to be triacetates which were completely substituted by three hydroxyl groups of cellulose monomers with three acetyl groups.

Table 7. Crystallinity Indices and Average Crystallite Sizes of Prepared WSC, WSCA-1, 2, 3 & 4 and SDC, SDCA-1, 2, 3 & 4

No.	Types of sample	I_{max}	I_{min}	I_c	Average crystallite sizes (nm)
1	WS Cellulose	21.971	14.370	**0.65**	**13.94**
2.	WSCA-1	21.682	17.441	0.80	21.41
3.	WSCA-2	21.472	17.556	0.80	21.63
4.	WSCA-3	22.770	17.420	0.77	26.26
5.	WSCA-4	22.941	17.501	0.76	29.12
6.	SD Cellulose	21.978	14.287	**0.65**	**21.42**
7.	SDCA-1	22.322	17.347	**0.78**	18.85
8.	SDCA-2	22.382	17.230	0.77	22.06
9.	SDCA-3	22.681	17.420	0.76	22.67
10.	SDCA-4	22.683	17.085	0.75	23.32

The Identification of WSCA-1 and SDCA-1 by NMR Spectroscopy with the Calculation of the Degree of Substitution

The following figures 7 and 8 indicates the ^{1}H NMR spectra of WSCA-1 and SDCA-1.

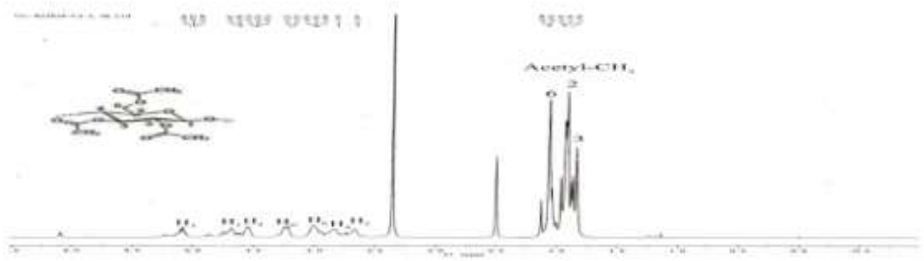


Figure 7. ^{1}H NMR spectrum of wheat straw cellulose acetate (WSCA-1)

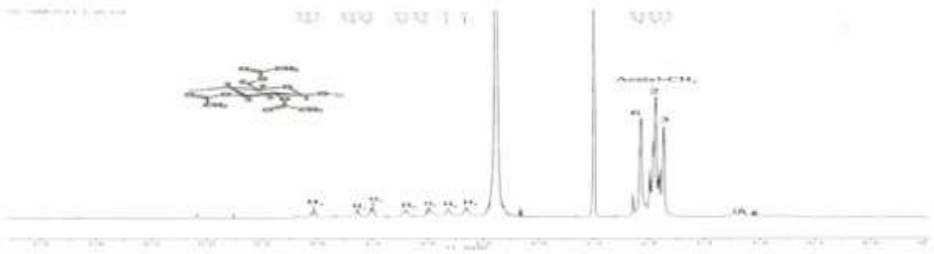


Figure 8. ^{1}H NMR spectrum of sawdust cellulose acetate (SDCA-1)

The following Tables 8 and 9 show ^{1}H NMR spectral data for WSCA-1 and SDCA-1.

Table 8. Chemical Shifts of ^{1}H NMR Signals for AGU Protons of WSCA-1 and SDCA-1 Compounds

Signals of AGU protons	Chemical shifts of WSCA-1 δ (ppm)	Chemical shifts of SDCA-1 δ (ppm)	Reference chemical shift * (δ) values
H-1	4.68	4.68	**4.70**
H-2	4.55	4.54	**4.61**
H-3	5.09	5.06	**4.97**
H-4	3.84	3.83	**3.72**
H-5	3.69	3.67	**3.68**
H-6	4.24	4.24	**4.30**
H-6′	4.00	4.02	**4.04**

AGU = Anhydroglucose unit (monomer of cellulose acetate)
***** Hiroyuki. *et al*., (2015)

Table 9. Chemical Shifts of ^{1}H NMR Signals for Acetyl Methyl Protons of C-6, C-2, C-3 of AGU of WSCA-1 and SDCA-1

Type of cellulose acetate	δ (ppm) of Acetyl-CH_3 protons		
	Me-6	**Me.2**	**Me-3**
WSCA-1	1.96	1.95	1.96
SDCA-1	1.91	1.86	1.89

Typical resonance characteristic of CH_3 groups at 2.2 to 1.5 ppm was reported by Hiroyuki *et al*., (2015). According to the Tables (8) and (9), ^{1}H NMR spectrum showed the peaks for 6 acetyl methyl protons at C-6 of AGU unit of WSCA and SDCA had the chemical shift values of 1.96 δ (ppm) and 1.91 δ (ppm), at C-2 had 1.95 δ(ppm) and 1.86 δ (ppm), at C-3 had 1.96 δ (ppm) and 1.89 δ (ppm). The signals for AGU protons are found in the range from 3.66 to 5.09 δ (ppm). These NMR signals confirm that the prepared WSCA-1 and SDCA compounds constitute the existence of acetyl methyl protons at carbon no. 6, 2 and 3 of AGU and that of each single proton on the AGU ring carbons.

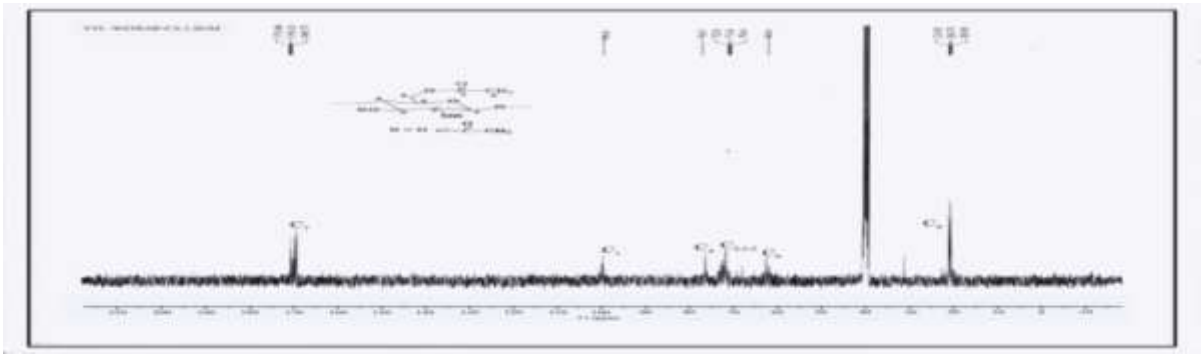


Figure 9 ^{13}C NMR spectrum of wheat straw cellulose acetate (WSCA-1)

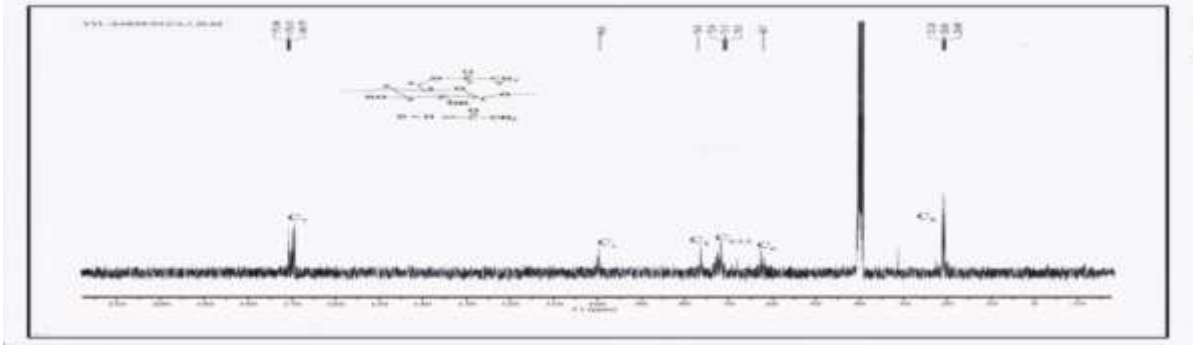


Figure 10. ^{13}C NMR spectrum of sawdust cellulose acetate (SDCA-1)

The above ^{1}H-decoupled ^{13}C NMR spectra indicate that the peaks for carbon number (1) to (5) on the ring carbons and carbon number (6) outside of the AGU ring compound and resonates at the respective chemical shifts. The complete acetylation occurs on carbon numbers 6, 2, and 3 by indicating the chemical shifts of about 21.0, 20.7, and 20.5 δ(ppm) for acetyl methyl carbons and also about 169.4, 170.1, and 171.1 δ(ppm) for acetyl carbonyl carbons at carbon number 6, 2 and 3 in WSCA-1 and the chemical shifts of about 21.2, 20.8, and 20.1 δ(ppm) for acetyl methyl carbons and 169.8, 170.1 and 171.1 δ(ppm) for acetyl carbonyl carbons on 6, 2, and 3 ring carbon atoms of AGU in SDCA-1 (Figures 9 and 10) The following Table 10 shows the signals for carbons in anhydroglucose unit and acetyl carbonyl carbons for each ^{13}C NMR spectrum in comparison with reference data.

Table 10. Chemical Shifts of ^{13}C NMR Signals for Ring Carbons with Their Substitutions of Acetyl Carbonyl Carbons (C-6, C-2, C-3) of AGU of WSCA-1 and SDCA-1

Signals of AGU carbons	Chemical shifts of WSCA-1, δ (ppm)	Chemical shifts of SDCA-1, δ (ppm)	Reference chemical shift*, (δ) ppm
C-1	99.8	99.9	**98.9**
C-2	70.4	70.3	**71.1**
C-3	71.8	71.5	**71.8**
C-4	76.5	76.8	**75.2**
C-5	72.8	72.6	**72.0**
C-6	60.4	60.7	**61.4**

*Hiroyuki et al., (2015)

Table 11. Chemical Shifts of ^{13}C NMR Signals for Acetyl Methyl Carbons and Carbonyl Carbons (C-6, C-2, C-3) of AGUs of WSCA-1 and SDCA-1

	Substituted position	Chemical shifts of acetyl methyl carbons δ (ppm)	Chemical shifts of carbonyl carbons δ (ppm)
WSCA-1	**C-6**	**21.0**	**169.4**
	C-2	**20.7**	**170.1**
	C-3	**20.5**	**171.0**
SDCA-1	**C-6**	**21.2**	**169.8**
	C-2	**20.8**	**170.1**
	C-3	**20.1**	**171.1**

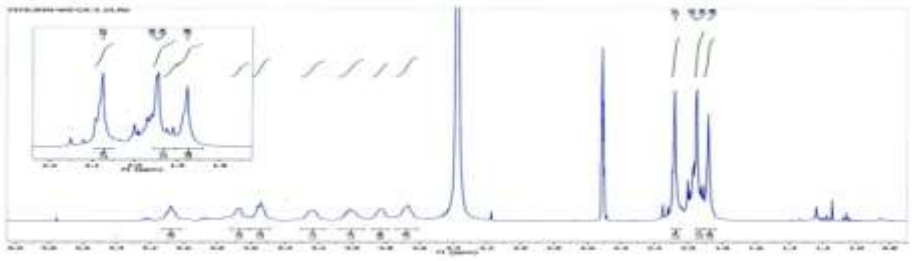


Figure 11 ^{1}H NMR spectrum showing the intensities of proton peaks of WSCA-1

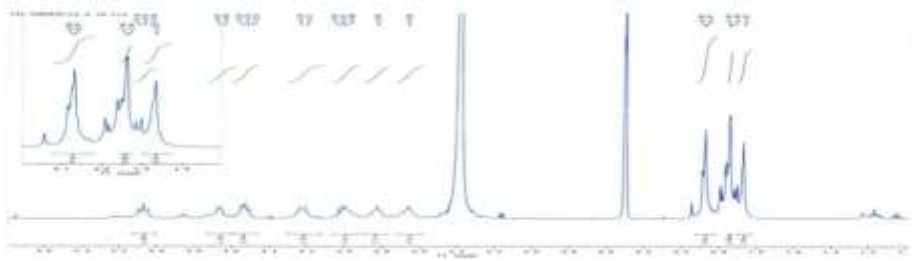


Figure 12. ^{1}H NMR spectrum showing the intensities of proton peaks of SDCA-1

In ^{1}H NMR spectrum of WSCA-1, the intensities for C-6, C-2, C-3 acetyl methyl protons were 2.74, 3.17, 2.66 and 3.41, 2.26, 2.45 in SDCA-1 spectrum. These had been confirmed that three protons of acetyl groups were attached to each acetyl methyl carbons. (Figures 11 and 12). The intensities for the ring protons were 1.38 attached at C-5, 0.96 at C-4, 1.26 at C-2, 1.01 at C-1 and 1.00 at C-3, 1.24 at C-6, 1.11 at C$^{/}$-6, outside of the AGU ring in WSCA-1. In SDCA-1, the intensities for the ring protons were 1.21 attached at C-5, 1.11 at C-4, 1.24 at C-2, 1.16 at C-1, 1.00 at C-3, and 1.31 at C-6, 1.27 at C$^{/}$-6, outside of the AGU ring. These data had been concluded that only one proton attached to each corresponding carbon in each cellulose acetate.

According to Cheng *et al.* (2010), the degree of substitution (DS) was calculated from the spectral intensities. The area of acetyl proton can be calculated by two-sides region between 1.9 to 2.2 ppm corresponds to three acetyl protons, the area of (AGU) ring protons can be calculated from two-sides region between 3.6 to 5.2 ppm corresponds to the seven (AGU) protons. The ratio of 1/3 of area of the acetyl protons to 1/7 of the area of the (AGU) protons gave the degree of substitution (DS). From the above ^{1}H NMR spectral data, the DS value of WSCA-1and SDCA-1 are listed in the following Table 12.

Table 12. Degree of Substitution Values for WSCA-1 and SDCA-1

Types of CA	Area of acetyl protons (cm^2)	1/3 of Area of Acetyl protons (cm^2)	Area of AGU ring protons (cm^2)	1/7 of Area of AGU ring protons (cm^2)	Degree of substitution (DS)
WSCA-1	9.46	3.16	7.41	1.06	2.98
SDCA-1	8.58	2.86	6.95	0.99	2.88

According to the values of DS obtained from calculations of titration data, FTIR, XRD and ^{1} H NMR and ^{13}C NMR spectral data, the prepared WSCA-1 and SDCA-1 were assumed to be triacetates.

Conclusion

In this research, the cellulose acetates were prepared according to the optimized acetylation method which provides the highest substitution of acetyl groups and the highest yield percent by four different time-limit sonication processes. Then the chemical and spectral analyses of prepared WSCAs and SDCAs were performed by acid-base titration, FT IR, XRD and NMR for the determination of the degree of substitution. From the titrimetric data, the optimized WSCA-1 has the DS values 3.04 and SDCA-1 has 2.79. So, these compounds can be regarded as cellulose triacetates. From the calculations by FT IR spectral data the value of DS for WSCA-1 is 3.00 and that for SDCA-1 is 2.98 that have confirmed that the prepared compounds are triacetates. Moreover, XRD informs that increasing crystallinity indices of acetates indicate the conversion of amorphous to crystalline nature and celluloses are completely converted to cellulose acetates. Then, the average crystallite sizes of these compounds are in the range of nanoparticle-size which are applied in the fabrication of cellulose acetate membrane. These WSCAs and SDCAs had been further identified by NMR spectroscopy. According to the ^{1}H NMR and ^{13}C NMR spectral data and the intensities of ^{1}H NMR spectral data, and the calculation of the values of DS (2.98. 2.88), the prepared WSCA and SDCA were found to be triacetates. In the sense of this research, agriculture byproducts and wastes can be made as the effective and valuable acetylated cellulose products for social needs. This paper reports the interested area for the fabrication of low-cost cellulose acetate based-products, cellulose acetate membrane which would be applied in the separation of hemoglobin variants by electrophoresis as a separating sheet or in wastewater treatment as the filtration membrane.

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