



Production of Acetyl Cellulose from Agricultural Waste of Oil Palm Empty Fruit Bunches

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In Indonesia especially in Lampung Province, there are a lot of oil palm empty fruit bunches (OPEFB) as an organic material waste. OPEFB is relatively inexpensive lignocellulose material as raw material of cellulose acetate or acetyl cellulose. In a business to bigger added value out of these natural renewable materials, the production of the acetyl cellulose was performed well by the acetylation of cellulose from OPEFB using different methods. These were extensively characterized using thermogravimetric analysis, Fourier transform infrared spectroscopy and X-ray diffraction. The results indicated that the acetyl cellulose resulted showed similar properties to cotton acetyl cellulose. Degree of substitution of the resultant acetyl cellulose from different methods was improved from 1.86 to 2.60.

Keywords: Oil palm, Empty fruit bunches, Acetyl cellulose, Acetylation.

INTRODUCTION

Acetyl cellulose or cellulose acetate is one of the main trade of cellulose material derivatives, rich is extensively performed in some applications such as a coatings, membrane, cigar filters, film and fibers. The acetyl cellulose was also found its utilization as material added in sheet and molded object and in surface coating and ink [1]. The acetyl cellulose is resulted by cellulose acetylation, in which cellulose reacts in the presence of acetic anhydride that is applied as acetylating agent, acetic acid employed as solvent [2,3]. Diacetate is the most populer applied acetyl celluloses, owning a degree of substitution (DS) over 2.8 [4].

Currently, cotton and wood are the raw material for production of acetyl cellulose. The use of cotton and wood as acetyl cellulose is expensive. It is important to understand that agricultural residues are the main raw materials prepared to human being for the continuous products. In recent years, several researchers have performed the production of acetyl cellulose from agriculture residue like rice hulls, wheat straws and corn stalk [5]. Filho and colleagues produced the cellulose triacetate through recycle newspaper and they informed water flux *via*

membrane [6]. Some other production methods were promoted for polysaccharide esterification, consisting of the use of ionic liquid [7], super acids [8], iminium chlorides and ring opening esterification [9]. Another recent investigation is the iodine application of the starch and cellulose esterification in the presence of acetic anhydride for catalyst [5,10].

In Indonesia especially in Lampung province, besides cassava peel [11] and algae biomass [12-15], in every year, oil palm empty fruit bunches commonly known OPEFB produce over 40 million tons of biomass waste on a wet basis [16]. In the palm oil mill, the OPEFB is a biomass waste and it contains lignocellulosic. The OPEFB can be reused as huge natural resources to be converted as valuable product like the cellulosic biomass obtained from biodegradable, inexhaustible, derivative, renewable and recyclable biopolymer [17]. The OPEFB as a lignocellulosic composite, it is composed of hemicellulose, lignin and compact cellulose with a cellulose fraction of 44.4 %. In addition, it can be converted to value-added acetyl cellulose. In this research, the synthesis of acetyl cellulose was carried out from OPEFB as raw material, the synthesis product obtained was investigated as function of cellulose time and characterized using the instruments such as FTIR, XRD, TGA and DTA.

EXPERIMENTAL

The oil palm empty fruit bunches (OPEFB) used in this work were taken from National Plantation Company (PTPN) palm oil mill in Lampung, Indonesia. The chemicals used, NaOH, H₂O₂, NaNO₂, HNO₃, Na₂SO₃, H₂SO₄ and acetic anhydride, were purchased from Alba Chemical. All chemicals were of reagent grade and used without further purification.

The chemical observation from functional groups existed in acetyl cellulose was investigated by using FTIR (Perkin Elmer spectrum series). The results of FTIR spectra were obtained since fifty times with scanning at resolution of 4 cm⁻¹ for the ranges of FTIR adsorption wavelength from 4000 to 450 cm⁻¹. The characterization of the sample by the instrument of X-ray diffraction (XRD), Bruker AXS Inc., Madison, WI, made in USA, with CuK_α radiation was applied at 30 kV and 15 mA to collect spectra data. Thermal stability of acetyl cellulose were investigated with using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) for the rate of heating 10 °C min⁻¹ under nitrogen atmosphere (Perkin Elmer TGA 7).

Preparation of OPEFB cellulose: The OPEFB was sliced to around 1 cm long, cleaned by water to separate dirt and unwanted materials, then air dried at approximately a moisture content for 10 % and kept in polyethylene bags. The OPEFB was placed in NaOH solution of 5 %, heated in a water bath at 80 °C for 1 h, filtered and cleaned to separate unwanted material. In the stage of bleaching, this material was inserted in the solution of 5 % NaOH and kept in water bath at 80 °C for 6 h. Delignification of fibers was obtained after purification and cleaned further with deionized water. Colour of the extract cellulose fibers was light yellow and they were re-suspended in 25 % H₂O₂ at 25 °C for 3 h. The pH was adjusted with NaOH solution (A sample). The cellulose fibers from A sample, then re-suspended in 25 % H₂O₂ for 3 h at 25 °C (B sample). For C sample, the OPEFB was suspended in 3 % HNO₃ solution and NaNO₂ (10 g) and placed in hot plate at 90 °C for 2 h. The extract cellulose was suspended using 2 % NaOH solution and 2 % Na₂SO₃ solution at 50 °C for 1 h. In bleaching step, extract cellulose was suspended with 10 % H₂O₂ solution for 1 h at 60 °C. While, D sample is commercial cotton. The white in colour of the suspension produced was screened, cleaned for several times and the insoluble part from cellulose was gained.

Synthesis of OPEFB acetyl cellulose: The acetylation of A, B, C, D cellulose was conducted using process described earlier from previous researchers [16,18,19]. An amount of 4 g from the OPEFB cellulose mixed with 100 mL of acetic acid were kept in a three-neck round-bottom flask adjusted with overhead stirrer. Stirring of the mixture was performed at 25 °C for 3 h, then over period of 5 min, the chemical mixtures containing sulfuric acid 0.3 mL, sodium bisulfate (2 g) and acetic anhydride (30 mL) were inserted into the mixture for acetylating process. With the constant stirring, the solution mixture was decanted little by little into 1 L of deionized water. The product obtained was filtered, cleaned and neutralized with deionized water.

RESULTS AND DISCUSSION

The characteristics of acetyl cellulose production under different methods are shown in Table-1. The α-cellulose composition from the isolate OPEFB cellulose was around 97.04 %

TABLE-1
PROPERTIES OF VARIOUS CELLULOSE
ACETATE SYNTHESIZED

Sample	α-Cellulose (%)	Acetyl cellulose (%)	Degree of substitution	Type	m.p. (°C)
A	71.77	13.56	1.86	Monoacetate	180
B	72.78	17.86	1.96	Monoacetate	181
C	97.04	38.74	2.60	Diacetate	170
D	98.57	41.11	2.70	Diacetate	185

(C sample), which is similar to the reported value of 97.1 % [19], but higher than 62.3 [20] and 93 % [17]. In addition delignification with using NaOH successfully isolated lignin and hemicellulose fraction and resulted a total cellulose yield of 79.0 % (w/w). The yield of this result are higher than other previous results informed yield around 44.4 [21] and 60.6 % [20], respectively.

The heterogeneous acetylation from OPEFB of acetyl cellulose was performed by using OPEFB cellulose with an over of acetic anhydride in presence of sulfuric acid and sodium bisulfate. The acetyl group might significantly with different of cellulose (A, B, C, D). The yield of acetyl cellulose maximum was obtained from C acetyl cellulose (38.7 %). The degree of substitution was affected significantly under different conditions. The maximum degree of substitution value was found 2.6 from C acetyl cellulose, which is nearly similar to the informed value of 2.8 [17], but this is lower than 2.8-3.0 [18].

FTIR spectra: Fig. 1 shows the spectra of FTIR from different acetyl cellulose samples. All the samples showed identical spectra appearance. The FTIR spectra describes reduction of frequency and band features of C=O at 1747, C-H at 1384 cm⁻¹ and -C-O at 1240 cm⁻¹, which are characteristics of acetyl cellulose. Comparing with the spectrum of D acetyl cellulose indicates that the material produced is indeed C acetyl cellulose. The broad absorption band located from 3500 to 3400 cm⁻¹ is because of stretching of -OH groups and the absorption band at 2900 cm⁻¹ is related to CH₂ group [22,23]. The FTIR spectra resultant acetyl cellulose show an identical trend to acetyl cellulose from commercial cotton. Nevertheless, the acetyl cellulose spectra of FTIR from commercial cotton present a sharp intensity band from the functional group of carbonyl at a round 1760 cm⁻¹, which parallel with the highest degree of substitution compared to the others.

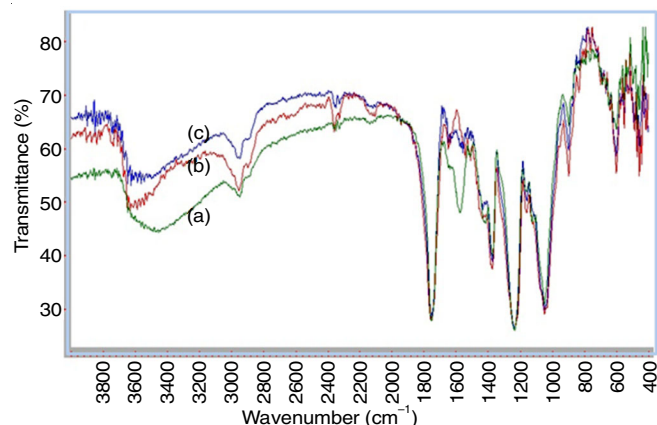


Fig. 1. FTIR spectra of various acetyl cellulose samples (a) B acetyl cellulose, (b) C acetyl cellulose and (c) D acetyl cellulose

XRD spectra: The XRD spectra of B acetyl cellulose, C acetyl cellulose and D acetyl cellulose are presented in Fig. 2. The XRD was applied to identify the crystalline nature from a material. Filho *et al.* [24] have reported a 2θ of 20.0. Nevertheless, all acetyl cellulose samples obtained have a sharp peak at 2θ of 8.5 and 23.0. The peaks with the strong high intensity indicates the crystalline nature of material while the value of intensity gives the number of crystalline structure. The diffractogram of the C acetyl cellulose showed peak with the big intensity crystalline at 2θ of 8.5 and 23.0, while the peak of amorphous material having intensity at 2θ of 15.0 and 20.0, respectively. These values correspond to the structure while the low intensity of amorphous peak were identified at a 2θ of around 13.0 due to the existence of cellulose acetate [18,25].

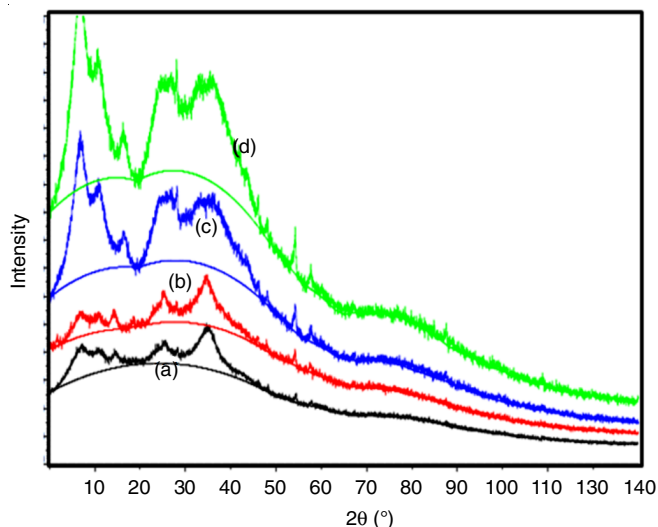


Fig. 2. X-ray diffractograms of acetyl cellulose (a) A acetyl cellulose, (b) B acetyl cellulose, (c) C acetyl cellulose and (d) D acetyl cellulose

Thermogravimetric analysis (TGA): Observing the thermal characteristics of reinforcing materials is urgent to study their application for composite processing at a high temperature [26]. Figs. 3 and 4 report TGA and DTA curves of B acetyl cellulose, C acetyl cellulose and D acetyl cellulose samples. Fig. 3 and 4 show that D acetyl cellulose began to degrade at 300 °C, then during the thermal degradation, the most apparent of weight loss occurred at 420 °C. C acetyl cellulose gave a lower initial degradation temperature of 250 °C while maximum degradation temperature of 390 °C in comparison to the D acetyl cellulose. In Figs. 3 and 4, it may be stated that the initial degradation temperature of B acetyl cellulose and C acetyl cellulose lower than D acetyl cellulose. The B acetyl cellulose, C acetyl cellulose and D acetyl cellulose gave two clear peaks indicating presence of two steps of degradation in material. In the B acetyl cellulose and D acetyl cellulose still exists hemicellulose and lignin, therefore they are not type of pure cellulose. The acetylation of this process on the B acetyl cellulose and D acetyl cellulose change the thermal characteristic of this material. It can be concluded that the low temperature from maximum degradation is because of the high hemicellulose contents, like hemicellulose in residues of pulp for thermal stability of acetyl cellulose [18].

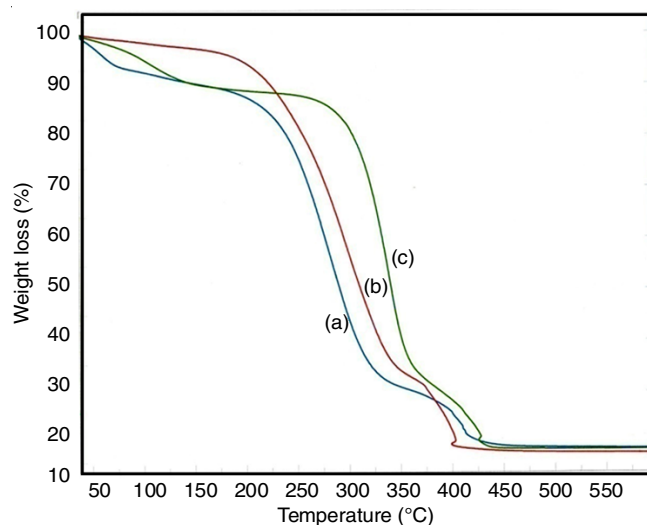


Fig. 3. Thermogravimetric curves of (a) B acetyl cellulose, (b) C acetyl cellulose and (c) D acetyl cellulose

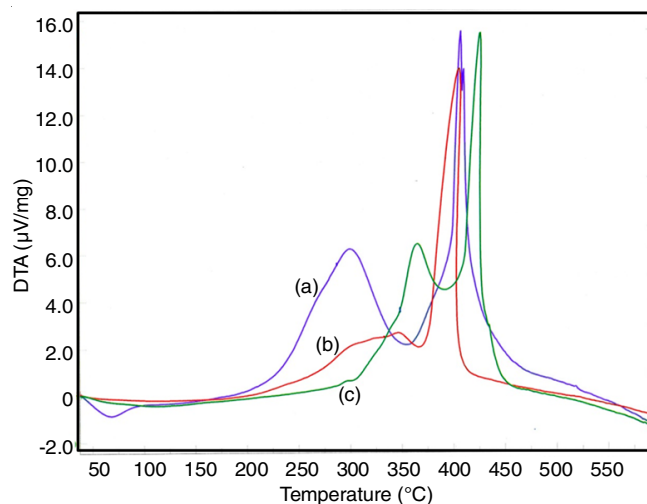


Fig. 4. Thermogram DTA of (a) B acetyl cellulose, (b) C acetyl cellulose and (c) D acetyl cellulose

Conclusion

This work is meant for new applications to control and use the agricultural waste. This work reports a process showing the transformation of much of the cellulose in OPEFB to acetyl cellulose. It is concluded that acetyl cellulose reaches a degree of substitution 2.6 obtained from C acetyl cellulose which was similar in major properties with D acetyl cellulose. Investigation with using instruments of FTIR, XRD and TGA prove that the acetylation of OPEFB acetyl cellulose runs successfully.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- H.N. Cheng, M.K. Dowd, G.W. Selling and A. Biswas, *Carbohydr. Polym.*, **80**, 449 (2010); <https://doi.org/10.1016/j.carbpol.2009.11.048>.
- J.F. Sassi and H. Chanzy, *Cellulose*, **2**, 111 (1995); <https://doi.org/10.1007/BF00816384>.
- K.J. Edgar, C.M. Buchanan, J.S. Debenham, P.A. Rundquist, B.D. Seiler, M.C. Shelton and D. Tindall, *Prog. Polym. Sci.*, **26**, 1605 (2001); [https://doi.org/10.1016/S0079-6700\(01\)00027-2](https://doi.org/10.1016/S0079-6700(01)00027-2).
- A. Biswas, B.C. Saha, J.W. Lawton, R.L. Shogren and J.L. Willett, *Cellulose*, **10**, 283 (2003); <https://doi.org/10.1023/A:1025117327970>.
- A. Biswas, B.C. Shah, J.W. Lawton and J.L. Willett, *Carbohydr. Polym.*, **64**, 134 (2006); <https://doi.org/10.1016/j.carbpol.2005.11.002>.
- G. Rodrigues-Filho, D.S. Monteiro, C.S. Meireles, R.M.N. de Assunção, D.A. Cerqueira, H.S. Barud, S.J.L. Ribeiro and Y. Messadeq, *Carbohydr. Polym.*, **73**, 74 (2008); <https://doi.org/10.1016/j.carbpol.2007.11.010>.
- J. Wu, J. Zhang, H. Zhang, J. He, Q. Ren and M. Guo, *Biomacromolecules*, **5**, 266 (2004); <https://doi.org/10.1021/bm034398d>.
- L. Yan, W. Li, Z. Qi and S. Liu, *J. Polym. Res.*, **13**, 375 (2006); <https://doi.org/10.1007/s10965-006-9054-x>.
- T. Heinze, T. Liebert and A. Koschella, *Esterification of Polysaccharides*, Springer: Berlin, pp. 41-116 (2006).
- A. Biswas, G. Selling, M. Appell, K.K. Woods, J.L. Willett and C.M. Buchanan, *Carbohydr. Polym.*, **68**, 555 (2007); <https://doi.org/10.1016/j.carbpol.2006.10.018>.
- Suharso and Buhani, *Asian J. Chem.*, **23**, 1112 (2011).
- B. Buhani, S. Suharso and Z. Sembiring, *Orient. J. Chem.*, **28**, 271 (2012); <https://doi.org/10.13005/ojc/280133>.
- F.B. Ahmad, Z. Zhang, W.O.S. Doherty and I.M. O'Hara, *Biofuels, Bioprod. Bioref.*, **10**, 378 (2016); <https://doi.org/10.1002/bbb.1645>.
- S.H. Chang, *Biomass Bioenergy*, **62**, 174 (2014); <https://doi.org/10.1016/j.biombioe.2014.01.002>.
- B. Buhani, S. Suharso and L. Aprilia, *Indo. J. Chem.*, **12**, 94 (2012); <https://doi.org/10.22146/ijc.21378>.
- M.D. Fauzi, M. Asad, M.N.M. Ibrahim and W.D. Wanrosli, *BioResources*, **9**, 4710 (2014).
- M.S. Nazir, B.A. Wahjoedi, A.W. Yussof and M.A. Abdullah, *BioResources*, **8**, 2161 (2013); <https://doi.org/10.15376/biores.8.2.2161-2172>.
- H.M. Shaikh, K.V. Pandare, G. Nair and A.J. Varma, ed.: R.L. Whistler, J.W. Green, J.N. Bemiller and M.L. Wolfram, *Cellulose Ester: Preparation, Properties, Reaction and Analyses: Cellulose Acetate, Method In: Carbohydrate Chemistry*, Academic Press: New York (2009).
- T. Ozaki, H. Ogawa and H. Sasai, *Cellulose Triacetates and Methods for Producing the Cellulose Acetate*, US Patent 6,683,174 (2004).
- W.D. Wanrosli, I. Mazlan, K.N. Law and R. Nasrullah, *Maderas Cienc. Technol.*, **13**, 193 (2011); <https://doi.org/10.4067/S0718-221X2011000200007>.
- R. Sun, J.M. Fang, L. Mott and J. Bolton, *J. Wood Chem. Technol.*, **19**, 167 (1999); <https://doi.org/10.1080/02773819909349606>.
- S.M.L. Rosa, N. Rehman, M.I.G. de Miranda, S.M.B. Nachtigall and C.I.D. Bica, *Carbohydr. Polym.*, **87**, 1131 (2012); <https://doi.org/10.1016/j.carbpol.2011.08.084>.
- M. Jahan, A. Saeed, Z. He and Y. Ni, *Cellulose*, **18**, 451 (2011); <https://doi.org/10.1007/s10570-010-9481-z>.
- G.R. Filho, S.F. da Cruz, D. Pasquini, D.A. Cerqueira, V.S. Prado and R.M.N. de Assunção, *J. Membr. Sci.*, **177**, 225 (2000); [https://doi.org/10.1016/S0376-7388\(00\)00469-5](https://doi.org/10.1016/S0376-7388(00)00469-5).
- H. Kono, Y. Numata, N. Nagai, T. Erata and T. Takai, *J. Polym. Sci., Part A Polym. Chem.*, **37**, 4100 (1999); [https://doi.org/10.1002/\(SICI\)1099-0518\(19991115\)37:22<4100::AID-POLA8>3.0.CO;2-D](https://doi.org/10.1002/(SICI)1099-0518(19991115)37:22<4100::AID-POLA8>3.0.CO;2-D).
- A. Alemdar and M. Sain, *Bioresour. Technol.*, **99**, 1664 (2008); <https://doi.org/10.1016/j.biortech.2007.04.029>.