Synthesis and Characterization of Cellulose Acetate from TCF Oil Palm Empty Fruit Bunch Pulp

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Cellulose acetate (CA) was successfully synthesized by the acetylation of TCF cellulose pulp from oil palm empty fruit bunches (OPEFB) at room temperature, using acetic anhydride as the acetylating agent and acetic acid as the solvent in the presence of sulfuric acid/sodium bisulfate as catalysts. Degree of substitution (DS) was controlled by the variables of acetylation time and acetic anhydride to cellulose ratio, under the heterogeneous state. The product (CA) obtained was characterized through Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimetry (DSC), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The results indicate that the CA obtained has characteristics similar to commercial CA, and DS is significantly dependent on acetylation time and the acetic anhydride-to-cellulose ratio.

Keywords: Acetylation; Cellulose acetate; OPEFB; TCF pulp

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INTRODUCTION

Cellulose acetate (CA), also known as acetyl cellulose, is one of the most commercially important cellulose derivatives, with a broad spectrum of applications in the fields of membrane processes such as dialysis, hemodialysis, reverse osmosis, and gas separation (Guilminot *et al*. 2007; Idris and Yet 2006; Sedelkin *et al*. 2006; Strathmann 2001; Wibowo *et al*. 2006; Yea *et al*. 2006), film coating (Entwistle and Rowe 1979), and textile industries (Reddy and Yang 2005). The most commonly used CAs include diacetate, having an average degree of substitution (DS) from 2.2 to 2.7, and triacetate, having an average degree of substitution (DS) above 2.8 (Heinze *et al.* 2003). These are excellent material choices for many films, fibers, and membranes, due to their excellent transparency and scratch resistance.

Presently, the raw material for the manufacture of cellulose acetate is composed of cotton and wood. Recent global trends suggest that the utilization of cotton and wood to produce cellulose derivatives, such as cellulose acetate, is expensive. In contrast, novel use of low-cost residual lignocellulosic biomass has become an attractive renewable resource because of its availability. During the past several years, many attempts have been made to prepare cellulose derivatives from agricultural by-products such as sugarcane bagasse (Filho *et al.* 2000; Liu *et al.* 2006), wheat straw (Sun *et al.* 2004), and rice hull (Biswas *et al.* 2006).

Oil palm empty fruit bunches (OPEFB) are lignocellulosic biomass and are obtained as waste from palm oil mills. OPEFB is a potential source of biomass for the production of cellulose due to its abundance, accessibility, and suitability. Indonesia and Malaysia have year to year estimated production of about 40 million tonnes (Fauzi and Wan Rosli 2011; Shuit *et al.* 2009; Sudiyani 2009). The high cellulose content of 60.6% in OPEFB (Wanrosli *et al.* 2004) represents a vast potential that could be exploited for high value-added products *via* conversion into cellulose derivatives, particularly cellulose acetate, which is the subject of this investigation. Because of environmental concerns associated with the use of chlorine and its derivatives, the OPEFB cellulose was prepared *via* a chlorine-free (TCF) bleaching sequence (Leh *et al.* 2008; Wan Rosli *et al.* 2003)

Various methods have been developed for producing CA, in which acetic anhydride and acetyl chloride are commonly used as acetylating agents. Industrially, CAs are generally produced by the reaction of cellulose with an excess of acetic anhydride in the presence of sulfuric acid or perchloric acid as the catalysts (Edgar *et al.* 2001; Steinmeier 2004). Because of the heterogenous nature of the reaction, it is impossible to synthesize partially substituted cellulose acetates directly (Cao *et al.* 2007). In this paper, we report the synthesis of CA from OPEFB TCF pulp by acetylation using $(CH_3CO)_2O/CH_3COOH$ in the presence of $H_2SO_4/NaHSO_4$ as catalysts. The purpose of using bisulfate as co-catalyst is to reduce the amount of sulfuric acid used. In addition, the acetylation process with bisulfate catalyst can be carried out effectively at low temperature (room temperature) (Kuo and Bogan 1997), which is an important factor when using low grade cellulose raw material such as OPEFB efficiently. The operation under room temperature is potentially more efficient, since a high operating temperature can cause some degradation of cellulose during the process. The chemical modification was observed as a function of acetylation time and characterized by FTIR, NMR, XRD, DSC, and SEM studies.

EXPERIMENTAL

Materials

Oil palm empty fruit bunches (OPEFB) were obtained for use in this study from a local palm oil mill in Perak, Malaysia. Before pulping, the OPEFB were cut to approximately 5 cm long, then soaked and washed with distilled water to remove dirt and unwanted materials, and air dried to an average moisture content of 12.5% and stored in polyethylene bags. Commercial CA was obtained from Sigma-Aldrich with a degree of substitution of 2.45 (acetyl content of 39.7%) and average molecular weight of 50,000. All the solvents and chemicals used were AR grade. Acetic acid (99.8%), acetic anhydride, sodium bisulfate, sulfuric acid (95 to 97%), sodium acetate, sodium hydroxide, and hydrochloric acid were obtained from E. Merck (Germany).

Methods

Preparation of oil palm empty fruit bunch (OPEFB) TCF Pulp

OPEFB pulp (subsequently termed OPEFB cellulose) was prepared using the environmentally benign process as described earlier by Wan Rosli *et al*. (2003) and Leh (2008). Basically, it involves water prehydrolysis of the OPEFB fibers, followed by soda-anthraquinone pulping. The unbleached pulp was bleached using a Total Chlorine Free (TCF) sequence of oxygen (O), ozone (Z), and peroxide (P) to a Kappa number of 1.6.

Kappa number is an indication of the residual lignin content or bleachability of wood pulp by a standardised analysis method such as T 236 om-99 (TAPPI 1999).

Synthesis of oil palm empty fruit bunch cellulose acetate (OPEFB-CA)

The acetylation of OPEFB cellulose was conducted using a process described earlier by Shaikh *et al*. (2009), Kuo *et al*. (1997), and Ozaki *et al*. (2004). OPEFB cellulose (5.0 g) and acetic acid (90 mL) were placed in a three-neck round-bottom flask fitted with an overhead stirrer. The reaction mixture was stirred at room temperature for 1 h and to this was added the acetylating mixture (acetic anhydride 20 to 30 mL, sodium bisulfate 0.1875 g, and sulfuric acid 0.125 mL) over a period of 0.5 h. In successive experiments, the reaction was carried out for 1, 2, 3, and 4 h, respectively. The sodium acetate solution (0.125 g) in aqueous acetic acid (10 mL) was added to the reaction mixture, and the stirring was continued for 15 min to remove the sulfate group substituent on the cellulose molecule. The reaction mixture was slowly poured into 1 L of distilled water with constant stirring. Once the precipitation process was completed, the product was filtered and washed with distilled water until the product was neutral.

Characterization Methods

The FTIR spectra of OPEFB cellulose, OPEFB-CA, and commercial CA samples were recorded on a Nicolet Avatar 360 Fourier-transform (FT)-IR instrument in the range of 500 to 4000 cm^{-1}. The samples were blended with spectroscopic grade KBr followed by pressing the mixture into ultra-thin pellets. The ^1H and ^{13}CNMR spectra were recorded on a Bruker Avance 500 and 100 MHz instrument, in which chemical shifts are reported in parts per million (δ-scale) from tetra methyl silane (TMS), taken as an internal or external standard in liquid (DMSO) and solid state NMR respectively. X-ray diffraction data were collected using a Bruker AXS X-ray diffraction instrument (Bruker AXS Inc., Madison, WI, USA) with CuKa radiation at 30 kV and 15 mA to investigate the XRD spectra. The scanning electron microscopy (SEM) was carried out using SEM Oxford INCA 400 model. Perkin Elmer instruments DSC4000 was used for thermal property analysis, in which about 10 mg sample was crimped in an aluminum pan and loaded along with reference pan without sample. The heating rate was 10 °C/min under a flowing nitrogen atmosphere and run up to 300 °C. The degree of substitution of cellulose was determined by the method described by standard method based on ASTM D871-96 (2010).

RESULTS AND DISCUSSION

Synthesis of Oil Palm Empty Fruit Bunch Cellulose Acetate (OPEFB-CA)

The heterogeneous acetylation of OPEFB-CA was carried out using high-purity OPEFB cellulose with an excess of acetic anhydride in the presence of sodium bisulfate and sulfuric acid as catalysts. During the acetylation reaction, some polar hydroxyl groups of OPEFB cellulose were substituted by acetyl groups. The acetyl group might significantly alter its properties due to solubility in organic solvents and more hydrophobic nature. The properties of OPEFB-CA synthesis under the same reaction conditions, but with different reaction times (1 to 4 h) and ratios of acetic anhydride to cellulose, are shown in Fig. 1. The degrees of substitution (DS) were significantly affected by both variables. In the acetylation rates for R4, the DS value was found at 2.65 after 2 h of reaction time, reaching the maximum DS value at 2.75 in 4 h. Thereafter, the DS value increased in the range of

2.25 to 2.75 with a reaction time of up to 4 h. The maximum DS value of R5 and R6 reached 2.87 and 2.94 after 4 h of reaction time, respectively. The reaction rate of R4 was faster than that of R5 and R6 in the DS range of 2.25 to 2.94 due to increased reaction time and acetic anhydride-to-cellulose ratio. Therefore, cellulose acetate samples using the reaction rates of R4, R5, and R6 showed no turbidity in solution and difference in reactivity between C2-OH and C3-OH. The first acetylating and favored position is expected to be C6-OH because this hydroxyl group is the least statically hindered with a lower DS value and is considered to be completely substituted.

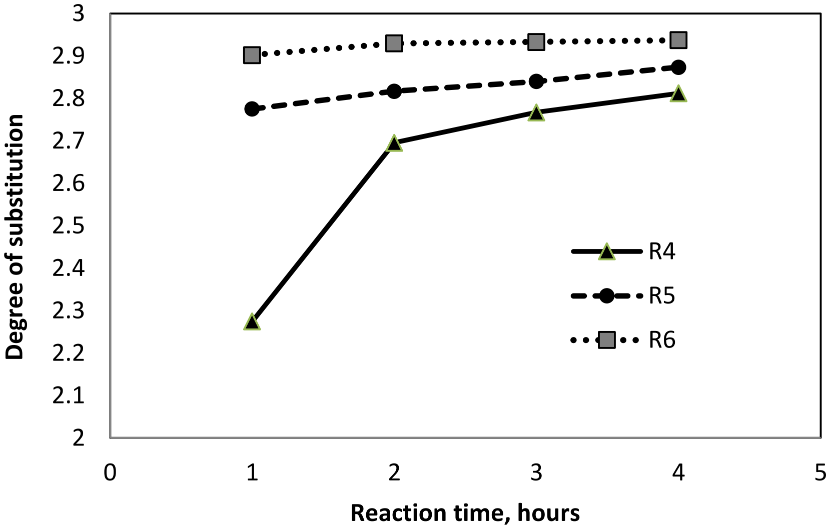


Fig. 1. Effect of reaction time and acetic anhydride-to-cellulose ratio on DS of OPEFB-CA. R4, R5, and R6 are acetic anhydride-to-cellulose ratios of 4, 5, and 6, respectively

FTIR Spectral Analysis

Figure 2 shows FT-IR spectra of OPEFB cellulose, OPEFB-CA, and commercial CA, indicated by a, b, and c, respectively.

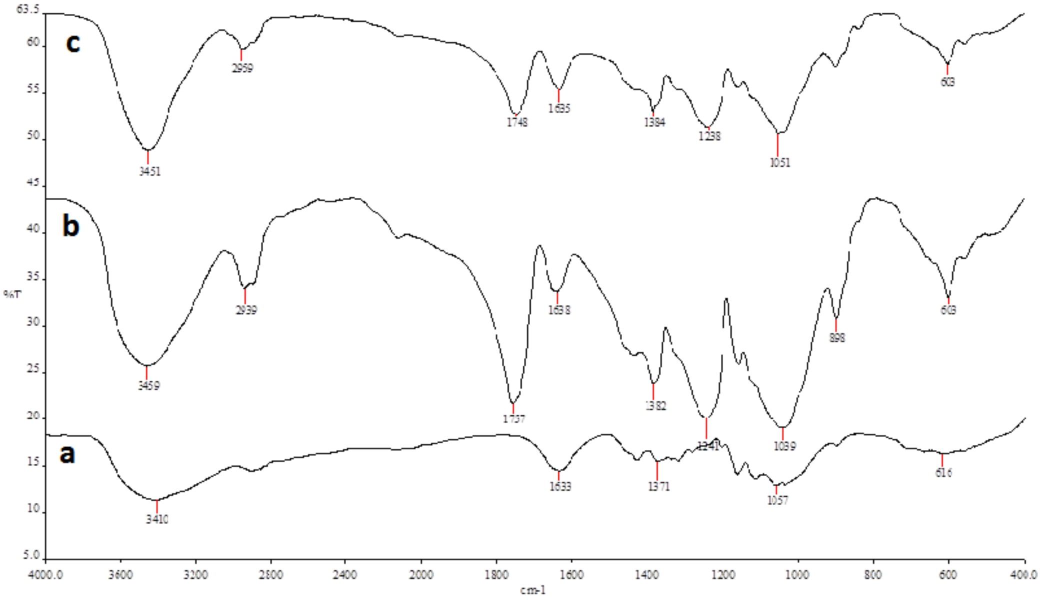


Fig. 2. FTIR spectra of (a) OPEFB cellulose, (b) OPEFB-CA with DS = 2.94, (c) commercial CA

The spectrum of OPEFB cellulose (Fig. 2a) shows the OH and C-H vibrations at 3410 and 1371 cm^{-1} distinctive of pure cellulose (Zhbankov 1966). The absorption band that appears at around 2950 cm^{-1} corresponds to the CH_2 group, and there is a moisture peak at 1635 cm^{-1} in all samples due to an interaction between cellulose and water (Rosa *et al*. 2012).

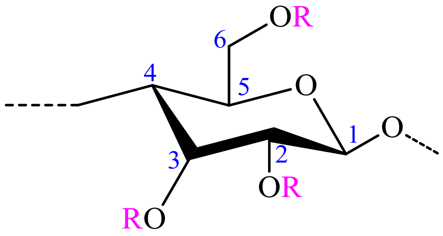
Figure 2b shows the IR spectrum of acetylated cellulose; there is an appearance of several new absorption peaks, such as those at 1748, 1384, and 1240 cm^{-1} corresponding to C=O, C-H and -CO- stretching of acetyl groups, which are characteristic of cellulose acetate. A comparison with the spectrum of commercial acetate (Fig. 2c) confirms that the product obtained was indeed OPEFB-CA. The absence of bands at 1760 to 1840 cm^{-1} and 1700 cm^{-1} confirms the absence of acetic acid and acetic anhydride, whereas the occurrence of a rather large absorption band at around 3450 cm^{-1} (OH stretching vibration) is probably due to the water molecules present in the cellulose acetate samples.

^{1}H and ^{13}CNMR Spectral Analysis

Proton nuclear magnetic resonance (^{1}H NMR) spectral studies were conducted on OPEFB-CA and commercial CA, as shown in Fig. 3. In the OPEFB-CA spectra with a DS value of 2.94, the proton signals appear to have chemical shifts similar to those of commercial CA. The spectrum shows five CH protons at δ 3.56 to 5.12 ppm, three acetyl-CH_3 protons at δ 1.88 to 2.08 ppm, and a CH_2 proton at δ 3.06 ppm. The signal appears at δ 2.50 to 2.51 and 3.36 ppm, which corresponds to the moisture and solvent (DMSO) peaks respectively. The moisture peak appears due to interaction between cellulose and water molecule during the acetylation (Goodlett *et al*. 1971). The ^{1}HNMR spectra of OPEFB cellulose and ^{13}CNMR spectra of cellulose acetates could not be run in DMSO because of the poor solubility. Therefore, the ^{13}CNMR spectra for all samples were recorded in the solid state (Fig. 4). Six carbon signals appear in the spectrum of OPEFB cellulose (Fig. 4a), in which three carbon signals, C2, C3, and C6, were attributed to the hydroxyl groups at 84.8, 76.0, and 66.2 ppm, respectively. The other carbon signals appear at 106.1, 89.9, and 73.4 ppm, corresponding to C1, C4, and C5, respectively. The hydroxyl groups at the C2, C3, and C6 positions exhibit different reaction activities, in which the hydroxyl group is substituted by the acetyl group during acetylation. In the ^{13}CNMR spectrum (Fig. 4b), the carbon signal of acetylated OPEFB-CA appears almost similar to chemical shifts of commercial CA (Fig. 4c). Thus, the signals that appear at δ 22.0 and 172.5 ppm are attributed to the three methyl (CH_3) and three carbonyl (C=O) carbons respectively. These methyl and hydrogen bonded carbonyl groups could not be assigned to the variable peaks due to spectral overlapping (Buchanan *et al*. 1991). In the same spectrum, the C1, C4, and C6 carbon signals appear at 101.6, 92.5, and 64.2 ppm respectively. However, the C2, C3, and C5 carbon signals appear at 75.1 ppm in a single peak attributed to the cellulose unit. It is also observed from the ^{13}CNMR spectra that the C4 signal on both the OPEFB -CA and commercial CA had disappeared, which is ascribed to the loss of crystallinity (Chunilall *et al*. 2012)

DSC Study

Results from the DSC study of OPEFB-cellulose, commercial CA, and OPEFB-CA samples are shown in Fig. 5. The endothermic peaks in all samples appearing in the range 30 to 120 ^{o}C are attributed to the evaporation of water (Scandola and Ceccorulli 1985) with a considerable shift of the position of the maximum peak temperature between the OPEFB cellulose and its acetylated form, with the former at 82.1 °C and the latter at 62.5 °C indicating that these biopolymers differ in their water holding capacity and also on their water-polymer interaction. Water molecules are held together by the cellulosic hydroxyl groups; however with acetylation, they are replaced by the acetate groups, thus rendering them more effective in their water holding capacity. In agreement with other previous studies, the peak in the vicinity of 230 °C can be assigned to the melting of the cellulose acetate crystalline region (Sun and Cabasso 1991; Kamide and Saito 1985). However, as can be seen from the figure, the melting endotherm for OPEFB-CA (at 232.4 °C) is higher than the commercial cellulose acetate at 214.2 °C, implying a greater thermal stability of the OPEFB-CA, which could be ascribed to the difference in their DS and also to the origins of the cellulosic source material of OPEFB TCF pulp. It is noteworthy to mention that in other OPEFB-CA samples with low DS value (not shown), the melting point endotherms are absent and being replaced with weak endotherms in the region of 170-180 °C which could either be either due to the presence of xylan diacetate in the sample as elaborated by Saka and Takanashi (1998) or can be attributed to the decomposition of the partly hydrolyzed cellulose (Barud *et al*. 2008).



OPEFB-Cellulose: R = H

OPEFB-CA/Commercial CA: R = $\underset{\underset{O}{\|}}{C}\,CH_3$

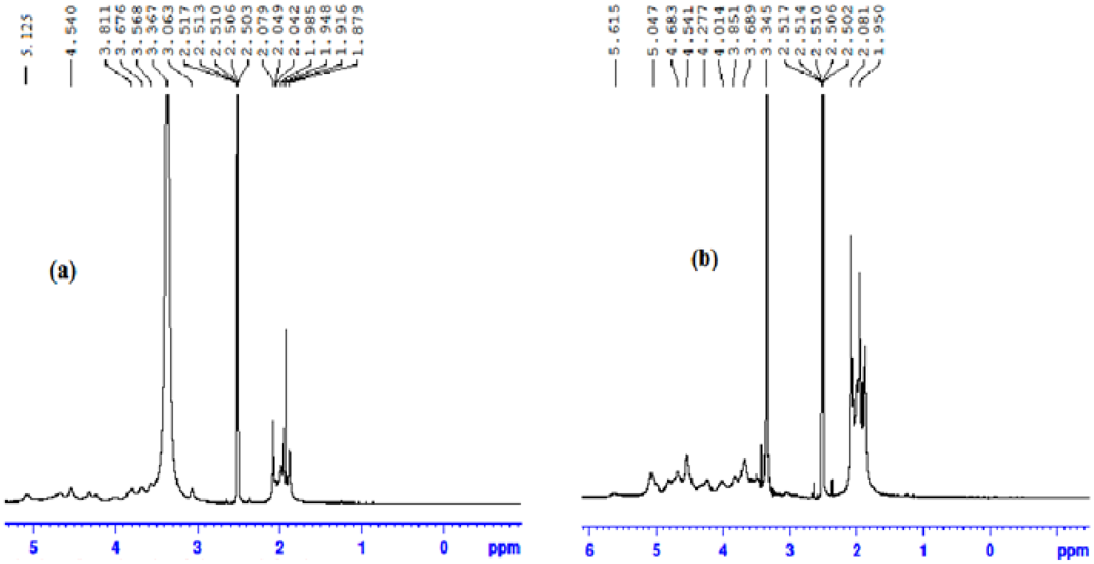


Fig. 3. ^{1}H NMR spectrum of OPEFB-CA with DS = 2.94 (a) and commercial CA (b) in DMSO-d6

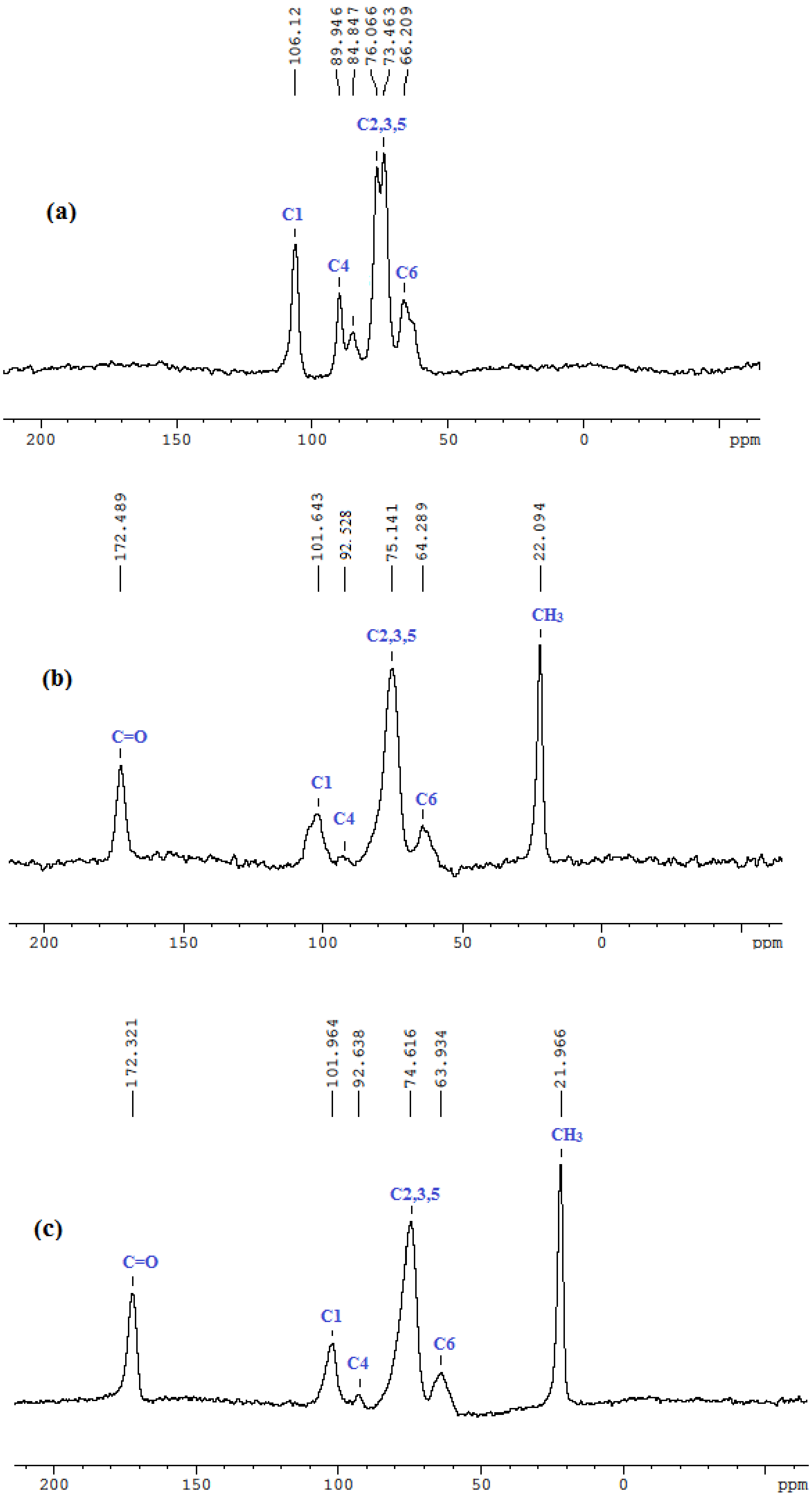


Fig. 4. ^{13}CNMR spectrum of OPEFB cellulose (a), OPEFB-CA with DS=2.94 (b), and commercial CA (c) in solid state

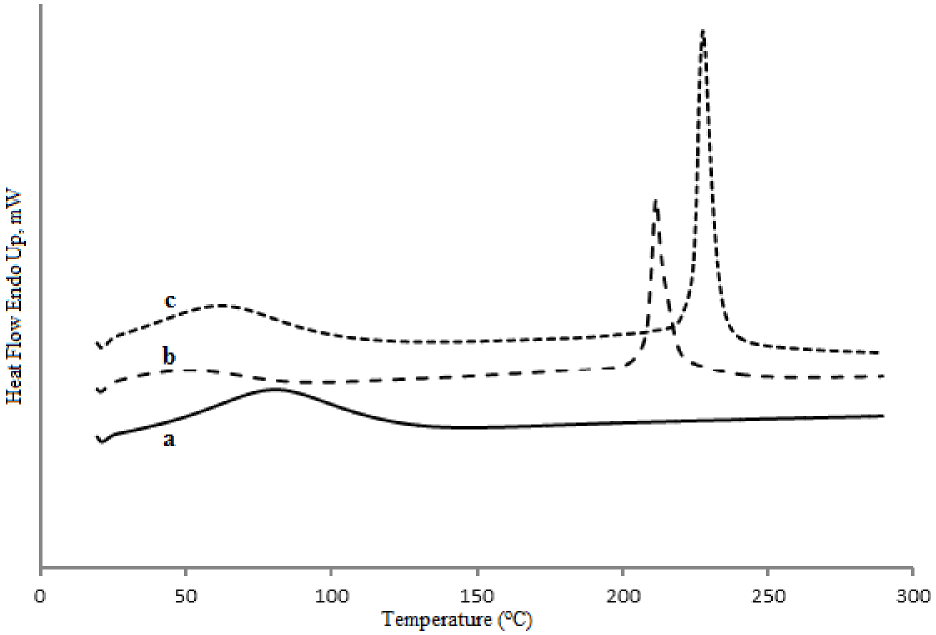


Fig. 5. DSC curves of (a) OPEFB-cellulose, (b) Commercial CA, & (c) OPEFB-CA with DS = 2.94

XRD Analysis

X-ray diffraction was used to determine the crystalline nature of the material. The spectra of OPEFB cellulose, OPEFB-CA, and commercial CA are shown in Fig. 6. The crystallinity index (*Cir)* was calculated using the following equation (Segal *et al*. 1959),

$$Cir = [(I_{002}\text{-}I_{am}/I_{002})] \times 100 \tag{1}$$

where I_{002} is the highest peak intensity of the crystalline fractions and I_{am} is the lowest intensity peak in the amorphous region.

The sharp high intensity peak describes the crystalline nature of the material, and the intensity value shows the amount of crystalline structure. The diffractogram of the OPEFB cellulose shows a high-intensity crystalline peak I_{002} at $2\theta = 22°$, and an amorphous peak with an intensity I_{am} at $2\theta = 18°$ corresponding to the crystallographic plane (Fig. 6a); therefore, only one broad peak was used in the calculation. The crystallinity index of OPEFB cellulose occurred at 74.6% due to its high intensity peak, while the amorphous portion causes the background noise line and occurs due to the removal of hemicellulose and lignin molecules (Li *et al.* 2009).

The crystallinity was decreased to 51.8% after acetylation of OPEFB cellulose, as shown in OPEFB-CA (Fig. 6b), in which only a weak-intensity and slightly crystalline peak appears at $2\theta = 14°$ due to the lower DS and reaction time. However, some low-intensity amorphous peaks were observed at a 2θ of around 13^{o} because of the presence of cellulose triacetate in OPEFB-CA (Kono *et al*. 1999).

The commercial CA (Fig. 6c) did not show any sharp or weak intensity peaks, which confirms its amorphous nature. The diminishing of the C4 signal (13C-NMR results) on the OPEFB-CA and commercial CA discussed earlier supports the XRD results regarding the loss of crystallinity of cellulose (Chunilall *et al*. 2012).

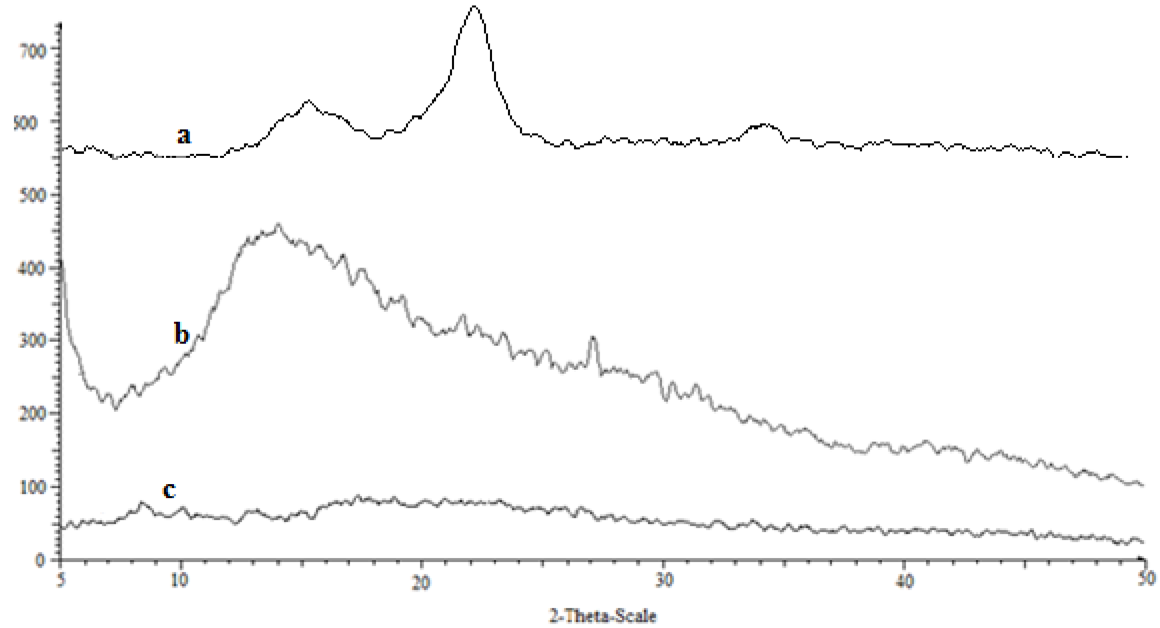


Fig. 6. XRD curves of OPEFB-cellulose (**a**), OPEFB-CA with DS=2.94 (**b**), and commercial CA (**c**)

CONCLUSIONS

1. The present study reports the synthesis and characterization of OPEFB-CA from totally chlorine free (TCF) pulp of oil palm empty fruit bunches (OPEFB) by acetylation using $(CH_3CO)_2O/CH_3COOH$ in the presence of $H_2SO_4/NaHSO_4$ as catalysts.
2. Spectral and morphological studies using FTIR, NMR, XRD, and SEM analyses indicate the successful acetylation of OPEFB-CA.
3. The degree of substitution (DS) can be controlled by reaction time and acetic anhydride-to-cellulose ratio, where the DS increased with increases in both process variables.
4. OPEFB-CA with a DS value of 2.94 obtained from OPEFB TCF cellulose was similar in major properties with commercial CA. XRD analyses indicate that the crystallinity of OPEFB TCF cellulose pulp decreases upon acetylation to OPEFB-CA from 74.6% to 51.8% with a higher thermal stability as compared to the commercial CA.

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