Cellulose Triacetate Synthesis from Cellulosic Wastes by Heterogeneous Reactions

Sherif S. Z. Hindi* and Refaat A. Abohassan

Cellulosic fibers from cotton fibers (CF), recycled writing papers (RWP), recycled newspapers (RN), and macerated woody fibers *of Leucaena leucocephala* (MWFL) were acetylated by heterogeneous reactions with glacial acetic acid, concentrated H_2SO_4, and acetic anhydride. The resultant cellulose triacetate (CTA) was characterized for yield and solubility as well as by using ^{1}H-NMR spectroscopy and SEM. The acetylated product (AP) yields for CF, RWP, RN, and MWFL were 112, 94, 84, and 73%, respectively. After isolation of pure CTA from the AP, the CTA yields were 87, 80, 68, and 54%. The solubility test for the CTA's showed a clear solubility in chloroform, as well as mixture of chloroform and methanol (9:1v/v) and vice versa for acetone. The degree of substitution (DS) values for the CTA's produced were nearly identical and confirmed the presence of CTA. In addition, the pore diameter of the CTA skeleton ranged from 0.072 to 0.239 μm for RWP and RN, and within the dimension scale of the CTA pinholes confirm the synthesis of CTA. Accordingly, pouring of the AP liquor at 25 °C in distilled water at the end of the acetylation and filtration did not hydrolyze the CTA to cellulose diacetate.

Keywords: Delignification; Acetylation; Cellulose triacetate; Solubility test; SEM; NMR

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INTRODUCTION

In Saudi Arabia, huge quantities of lignocellulosic municipal wastes (writing paper and newspaper) are generated annually from cities and agro-wastes from agricultural spaces. These wastes can be reprocessed to extract cellulosic precursors for the production of cellulose derivatives. This recycling is important not only for diminishing the environmental hazards arising from the decay of the wastes but also for obtaining valuable products. Agricultural residues can be used as abundant, low-cost feedstock either for the production of fuel ethanol or for hydrolyzing hemicelluloses into monomeric sugars for the conversion into ethanol or cellulose acetate, by acetylation of the cellulosic byproducts (Biswas *et al.* 2006).

High-yield fiber plants offer enormous potential in the pulp and fiber manufacturing sector (Mansfield and Weineisen 2007). Leucaena is the most common multipurpose leguminous tree due to its suitability to stabilize sloping soils and green manure as well as its adaptation to a wide range of soil and conditions (Aref 2005). In addition, *Leucaena leucocephala* is promising as a faster growing species for biomass and paper production, and it has shown suitable physical characteristics for paper sheet production (Lopez *et al.* 2008). Furthermore, this species was found to be the best resource for fiber production due to its high content of holocelluloses and low extractives, lignin and ash. In addition, it has an acceptable fiber length and specific gravity, which is comparable to that of hardwoods (Hindi *et al.* 2010).

Cellulose derivatives have gained attention worldwide due to their abundance and biodegradability as well as having a lower environmental impact compared with fossil based polymers (Zhang 2007). Cellulose acetate (CA) is a commonly used cellulose derivative with many applications, such as coating, filming, membranous filters, textiles, high absorbency-products, thermoplastics, sheets for food packaging, cosmetics, pharmaceuticals, and hypoallergenic surgical products (Tang *et al.* 1997; Edgar *et al.* 2001; Heinze and Liebert 2001; Cao *et al.* 2007; Zhang 2007; Fischer *et al*. 2008; Cheng *et al.* 2011).

The acetylation process is one of the most efficient derivatizations of cellulose. Industrially, almost all cellulose acetates, with the exception of fibrous cellulose triacetates (CTA), are synthesized using a solution of sulfuric acid as the catalyst and acetic anhydride in an acetic acid solvent (Tang *et al.* 1997; Hummel 2004). It was found that the acetylation of the pulp in an acetic anhydride/ethanolic acid solvent and H_2SO_4 catalyzed solution yielded cellulose di- and tri-acetates (Israel *et al*. 2008). The thermally stable cellulose acetate membranes were produced from recycled newspaper and comparable to those produced by a commercial CA (Filho *et al.* 2008).

The acetylation of cellulose with an acetic anhydride and iodine solution proved to be more effective than using a mixture of acetic acid, acetic anhydride, and sulfuric acid as solvents (de Paula *et al.* 2008; Cheng *et al.* 2010; Das *et al.* 2014). Crude cotton burrs and cottonseed hulls were converted into CAs without any pre-treatment by acetic anhydride and iodine. The CA yield from these resources was 15 to 24% based on the pure cellulose in the parent crude material, and was 50 to 80% based on the pure cellulose in that parent resource (Cheng *et al.* 2010). It was found that pre-heating the substrates with dilute sulfuric acid to remove the hemicellulosic sugars increased the yield of CA greatly, rendering the cellulose more accessible and reactive towards acetylation (Biswas *et al.* 2006).

For CA obtained under heterogeneous conditions, the acetylated hemicelluloses act as an internal plasticizer (Shaikh *et al.* 2009). In addition, before using acetic anhydride and phosphotungstic acid for cellulose acetylation, Fan *et al.* (2013) found that removal of hemicellulose and lignin from the crude material was affected by KOH concentration and the immersion time in acetic acid. The CA was synthesized from ramie fiber using acetic anhydride (1:6 w/w) in acidic condition at 80 °C for 0.5 to 1 h (Liu *et al.* 2007). The previously water-soaked flax fibers were acetylated using toluene, acetic anhydride, and perchloric acid (60%) at 60 °C for l to 3 h (Bledzki *et al.* 2008).

The CA was successfully synthesized using the acetylation of cellulose pulp from oil palm empty fruit bunches at ambient temperature, using acetic anhydride and acetic acid in the presence of sulfuric acid/sodium bisulfate catalysts (Djuned *et al.* 2014). The degree of substitution (DS) was significantly dependent on acetylation time and the acetic anhydride-to-cellulose ratio. In addition, Cao *et al*. (2010) synthesized CA with DS ranging from 0.4 to 3.0 without a catalyst, by using an ionic liquid in one step. In addition, cellulose diacetate (CDA), with DS = 1.98 and CTA (DS = 2.79), was produced from newspaper waste *via* a homogeneous acetylation procedure (Filho *et al.* 2008).

The acetylated product can be bleached without loss of acetyl content to eliminate insoluble lignin by a mixture of dichloromethane and methanol or acid chlorite treatment (Barkalow *et al*. 1989). Since some cardboards possess high lignin, hemicellulose, and ash contents, it is not suitable for synthesizing cellulose derivatives (Loo *et al*. 2012).

This is because the acetylation of pulps containing more than 5% hemicellulose will produce hemicellulose acetates, such as xylan acetate and glucomannan acetate, consequently resulting in industrial problems such as poor filterability, turbidity, and false viscosity (Ueda *et al*. 1988; Matsumura and Saka 1992). In addition, high lignin content reduces the accessibility of hydroxyl content of cellulose.

The yield of CA produced is the ratio between of the resultant CA compared with the weight of the parent cellulose at the beginning of the acetylation process (Bahmid *et al.* 2013). Based on a parent cellulose content of 75 to 80 % and an acetylated product ranging from 103 to 150%, the amount of CA synthesized would equal 66% when using the catalysts acetic anhydride and iodine in an eco-friendly, solvent-free condition (Barkalow *et al.* 1989; Das *et al.* 2014). The CA yields were approximately 15 to 24% of the oven-dry crude biomass (cotton burr and cottonseed hull), and 50 to 80% of the pure cellulose in the parent material (Cheng *et al.* 2010). Without the pre-treatment, the CA conversions from wheat straw, corn fiber, and rice hulls were 0.5, 1.8, and 13.5 wt%, respectively. After pre-treatment, the conversion rate increased to approximately 25 wt% (Biswas *et al.* 2006).

The yield of CDA for 14 agricultural wastes varied from 17 to 44%, while the CTA yield ranged from 35 to 62% (Israel *et al.* 2008). The yield of CTA value was higher than CDA due to the partial acetylation in CDA and the full acetylation of cellulose in CTA (Browning 1997 and Israel *et al.* 2008). Furthermore, Bahmid *et al.* (2013) produced CA in good yields between 57.25 to 189.69%. It was indicated that the longer the acetylation process, the higher the CA yields obtained. The average yields of CDA and CTA were 57% and 117.47%, respectively (Akpabio *et al.* 2012).

Studies of morphological and anatomical structure of CTA shows the influence of acetylation conditions on the reaction mechanism (Cheng *et al.* 1994; Tang *et al.* 1997). For low temperature acetylation (45 °C), the reaction occurred in the segregated micropores on the surface of cellulose (Tang *et al.* 1997).

The objective of this investigation was to study the possibility of using cellulosic waste in Saudi Arabia as resources for CTA synthesis. These resources were recycled writing papers (RWP), recycled newspapers (RN), macerated woody fibers of *Leucaena leucocephala* (MWFL), and Egyptian cotton (*Gossypium barbadense* L.) fibers (CF).

EXPERIMENTAL

Raw Materials

Imported Egyptian medical cotton, made by Al-Mahalla factory, was selected as a pure cellulosic reference. The RWP and RNs were collected from the Scientific Endowment of King Abdullaziz University. *Leucaena leucocephala* was chosen as a crude resource for the woody fibers. Twelve healthy shrubs of the Leucaena plantation, grown at the Agricultural Research Station (ARS), Hada Al-Sham, King Abdul-Aziz University, about 120 km northeastern of Jeddah, were chosen randomly. The shrubs selected from the Leucaena plantation were 3-years old, and the diameter varied from 10 to 15 cm. The selected shrubs were cut at 20 cm above the ground level for the maceration process. From each of the 12 shrubs, one healthy branch was taken randomly. From each selected branch, one disc of about 40 cm was cut at a height of 10 cm above the branch base. After discarding the pith and bark, the remaining volume of the disc was cross cut into pieces (2 cm). Then, the wood pieces were longitudinally cut into thin chips

(2 cm × 1mm) using a knife press. The wood chips were divided into two equal portions: the first portion was assigned to the maceration process required for cellulosic fiber production, while the second was used for the chemical characterization of wood contents (*e.g.*, total extractives, lignin, holocelluloses, and ash).

Samples Preparation

Cotton fibers were crosscut into small pieces using scissors to ease the stirring of the acetylation reagents. Each of the RWP and RN sheets were reduced into snippets using a mechanical scissor immersed in distilled water, and the snippets were blended until a jelly-like texture was formed. Their fibers were washed several times using distilled water to remove all additives and fillers that were added during manufacturing. The fibers were filtered, air-dried, oven dried at 100 °C, and stored until further use.

The wood chips of leucaena assigned for use in the chemical characterization of the wood were ground to a size that was able to pass through a 40-mesh sieve and were retained on a 60-mesh sieve. Then, they were specified for the determinations of total extractives content (TEC), lignin content (LC), holocelluloses content (HC), and ash content (AC). For each determination, three samples were taken at random from each tree. Accordingly, 36 samples of leucaena were specified for holocelluloses and ash contents. Furthermore, an additional 36 samples were assigned for both total extractives content and subsequent lignin content determinations.

Wood Pretreatments

Elimination of total extractives

This process was repeated for all leucaena wood samples to eliminate the organic chemicals that may interfere with the maceration reagents used (Hindi *et al*. 2010), according to the ASTM (1989b) standard.

Delignification by the Franklin method

Five grams of thin chips from each leucaena tree were digested separately in a solution of hydrogen peroxide (35%) and glacial acetic acid in a ratio of 1:1 and kept in an oven at 60 °C for 48 h. The macerated samples were removed, disintegrated, washed, air-dried, and stored until the heterogeneous acetylation process.

CTA Synthesis

Preparation of the CTA was achieved by combining 2.0 g of each of the cellulosic resources with 35 mL of glacial acetic acid. The solution was kept in a water bath between 50 and 55 °C for 1 h with frequent stirring. An acetylating mixture of 0.4 mL concentrated H_2SO_4 and 10 mL of acetic anhydride was gradually added to the glacial acetic acid-pulp mixture, keeping the temperature at 60 ± 5 °C. The resulting mixture was kept in water bath for 1 h at 50 to 55 °C with continuous stirring until a clear solution was obtained. The solution was poured in distilled water to reduce the pH. The precipitate was filtered through, washed thoroughly until it was neutral to litmus, and dried.

Isolation of Cellulose Triacetate by Differential Solubility

Pure CTA was isolated from the acetylated products (AP) by differential solubility. The AP was stirred in a 40 mL dichloromethane/methanol (9:1, v/v) solution for 2 h. The soluble fraction was isolated using filtration through Whatman no. 4 filter paper, concentrated to 15 mL, and precipitated in 50 mL of n-hexane. The precipitate was washed with 95% absolute ethanol and dried at 60 °C under a vacuum.

Characterization of Cellulosic Resources

The properties studied were: fiber length (FL), fiber width (FW), and fiber yield (FY) of the crude fibers, total extractives content (TEC), lignin content (LC), holocelluloses content (HC), and ash content (AC). For the FL and FW measurements, one drop of the bleached fibers was stained with 1% aqueous safranine and mounted on a slide to measure the FL. The fibers were speculated using a light microscope (CE-MC200A) with a suitable visualization and photography system (OPTIKA PRO 5 Digital Camera- 4083.12) and a calibrated eyepiece at 10X magnification. Twenty measurements were taken for each slide as described by Hindi *et al.* (2010).

Scanning electron microscopy (SEM) was used to measure the pore diameter of the cellulosic fibers precursors. The samples were placed on double sided carbon tape on an Al-stub and air-dried. Before examination, all samples were sputter-coated with a 15 nm thick gold layer (JEOL JFC- 1600 Auto Fine Coater) in a vacuum chamber (Tang *et al.* 1997). The samples were examined with a Quanta FEG 450, FEI SEM (Netherlands).

Through the chemical determinations of the leucaena wood samples (one gram each), total extractives content (TEC) was measured in accordance with the ASTM (1989b) standard. The samples were extracted through a tertiary stage using ethanol-benzene (1:2), ethanol, and hot water in a Soxhlet apparatus according to ASTM (1989b). The same samples were delignified after extraction according to the ASTM (1989c). The samples were primary-hydrolyzed using H_2SO_4 (72%), and then secondary-hydrolyzed under an adjusted concentration of H_2SO_4 (3%) using a refluxed condenser. After the filtration process using Watman no. 44 filter paper, the brown precipitate was washed well of any acid traces, air-dried, and oven-dried, after which, lignin content (LC) was determined. In addition, the holocellulose content (HC) of the woody fibers of leucaena was determined according to Viera *et al*. (2007), as follows. A fiber concentration of (5% wt) was prepared in a round bottom flask. Then, 0.5 mL of glacial acetic acid and 0.75 g of sodium chlorite were added. The flask was stoppered to prevent the loss of gas released during the reaction process. Then, the contents were placed in a water bath at 75 °C. After each hour, 0.5 mL acetic acid and 0.75 g of sodium chlorite were added to the flask, repeating this step twice. The system was cooled to 10 °C, and then filtered in a previously tarred fritted funnel and washed with distilled water at 5 °C until the fibrous residue became whitish. The funnel containing the fibrous residue was then dried in an oven at 105 ± 5 °C for 6 h. After this period, the residue was cooled to room temperature in a desiccator and then weighed to quantify the holocelluloses. Furthermore, to determine the ash content (AC) of the wood, one gram of each oven-dried sample was ignited at 600 °C until all of the carbon was eliminated (ASTM 1989a).

Characterization of CTA

The properties studied for the acetylated resources were CTA yield, the degree of substitution (DS), the pore diameter (PO) of the skeleton, and a solubility test in chloroform, acetone, and a mixture of chloroform and methanol (9:1 v/v). In addition, ^{1}H-NMR was used to estimate the degree of substitution (DS), and SEM was used to estimate pore diameter of the CTA membrane (Tang *et al.* 1997 and El-Saied *et al.* 2003; Hummel 2004; Israel *et al.* 2008).

The NMR spectra were obtained on a DRX400 spectrometer from Bruker Instruments (Germany). Standard instrument conditions were used for ^{1}H-NMR using deuterated chloroform ($CDCl_3$) as the solvent. All chemical shifts were referenced to tetramethylsilane at 0 ppm. For a typical ^{1}H-NMR spectrum, the area between 3.6 and 5.2 ppm corresponded to the seven anhydroglucose protons, and the area between 1.9 and 2.2 ppm corresponded to the three acetyl protons. The ratio of 1/3 of the acetyl area to 1/7 of the anhydroglucose area gave the DS. The DS was calculated from the spectral intensities that resulted from the ^{1}H-NMR (Cao *et al.* 2007; Peres de Paula *et al.* 2008; Cheng *et al.* 2010).

SEM Measurements

Oven dried-CTA powder with a particle size of about 149 µm was sputter-coated with a 15 nm thick gold layer (JEOL JFC- 1600 Auto Fine Coater) in a vacuum chamber and was used for the SEM visualization. The pore diameter (PD) measurements were achieved using the SEM images obtained by using Quanta FEG 450, FEI SEM (Netherlands) at an accelerating voltage of 5 kV for the CTA produced from each of the cotton (Fig. 8), recycled paper, (Fig. 9), and recycled newspaper resources (Fig. 10), and at 10 kV for CTA produced from the *Leucaena* (Fig. 11) and at 20 kV for the cellulosic precursors (Fig. 2 and 3).

Solubility Test

The solubility test for the acetylated product (AP) was conducted in each of acetone, chloroform and a mixture of chloroform and methanol in a ratio of 9:1, v/v (Akpabio *et al*. 2012). From each of the four cellulosic resources, nine AP samples (about 1 g each) were assigned for this test to represent the three replicates used. The oven-dried AP samples were ground to a suitable particle size (149 µm) were allowed to dissolve in each solvent for about 30 min at ambient temperature with continuous stirring.

Statistical Design

A complete randomized block design with three replications was used in this investigation. Statistical analysis of the recorded data was done according to Dancey and Reidy (2007) using the analysis of variance (ANOVA) procedure and least significant difference test (LSD) of the means. Significance was accepted at $P < 0.05$.

RESULTS AND DISCUSSION

The properties studied of the four crude cellulosic resources, namely, fiber yield (FY), fiber length (FL), fiber width (FW), total extractives content, holocellulose content (HC), and lignin content (LC) are listed in Tables 1 and 2, while their SEM images are presented in Fig. 1 and 2.

The statistical analyses indicated that the four resources were significantly different in their properties (Table 1). The CF, RWP, and RN resources yielded higher FY values of 97, 84, and 81%, respectively, because of their increased cellulose content. On the other hand, MWFL had the lowest yield of 67%, which was based on the crude cellulosic content.

Table 1. Mean Values[1] of Fiber Yield (FY), Fiber Length (FL), Fiber Width (FW) of the Cellulosic Resources

Crude cellulosic resources	FY[2] (%)	FL[3] (mm)	FW[2] (μm)
CF	97.11^{a}	26^{a}	12.23^{bc}
RWP	84.76^{b}	1.33^{b}	10.88^{c}
RN	80.97^{b}	2.74^{b}	13.63^{bc}
MWFL	67.46^{c}	1.13^{b}	24.18^{a}

[1] Means within the same column followed by the same letter are not significantly different according to LSD at $P < 0.05$
[2] Each value is an average of 12 samples
[3] Each value is an average of 240 total observations
CF: cotton fibers; RWP: recycled writing papers; RN: recycled newspapers; MWFL: macerated woody fibers of *Leucaena leucocephala*

The CF fibers yielded the highest FL values (mean 26 mm), while the MWFL and RWP fibers had the shortest lengths (mean 1.13 and 1.33 mm, respectively), and the fibers of the RN had a mean FL value of 2.74 mm. The MWFL fibers had the highest FW value of 24.18 μm, whereas RWP had the lowest FW value of 10.88 μm, as shown in Table 1 and Fig. 1. The variation between cellulosic resources in both the FL and FW properties could be attributed to their botanical origin as well as fiber maceration process used. For instance, thermomechanical processing and refining used for preparation of newspaper fibers can reduce the fibre length (FL).

Chemical characterization presented in Table 2 was important to interpret the higher yields of the acetylated products comparing with those of the CTA (Table 3). The acetylated product represent all of the parent chemical constituents that were totally, partially, or not acetylated from the parent cellulose, such as lignin, hemicelluloses, and some organic extractives. Accordingly, purification of the parent cellulosic resource was an essential step in maximizing the CTA product yield (CTAY).

Table 2. Mean Values[1,2] of Total Extractives Content (TEC), Holocelluloses Content (HC), Lignin Content (LC), and Ash Content (AC) of the Four Crude Cellulosic Resources

Crude cellulosic resources	TEC (%)	HC (%)	LC (%)	AC (%)
CF	NIL	98.11^{a}	NIL	0.466^{b}
RWP	NIL	85.68^{b}	3.12^{c}	10.2^{a}
RN	NIL	83.16^{b}	7.22^{b}	9.62^{a}
MWFL	9.74^{a}	70.82^{c}	18.64^{a}	1.22^{b}

[1] Means within the same column followed by the same letter are not significantly different according to LSD at $P < 0.05$
[2] Each value is an average of 36 samples
CF: cotton fibers; RWP: recycled writing papers; RN: recycled newspapers; and MWFL: macerated woody fibers of *Leucaena leucocephala*

According to the TEC yields (Table 2), the MWFL fibers had the highest (9.74%), while the other resources had negligible amounts. In addition, the CF had the highest amount of the HC (98.11%), whereas the MWFL had the lowest amount (70.82%). The recycled fibrous resources (RWP and RN) had HC values that were notably similar. For the LC, the highest yield was in the MWFL samples (18.64%), while the CF was an ideal precursor that did not contain any LC. The RWP and RN samples were found to have 7.22% and 4.12% LC, respectively. The difference between the RWP and RN can be attributed to the pulping technique used to prepare them, whereby RWP was macerated using a chemical pulping process, while most of the RN was produced using a mechanical process. Furthermore, the highest AC values were contained in both RWP and NP because of the inorganic compounds added to them. Meanwhile, the manufacturing process enhanced their qualities. On the other hand, CF and MWFL had lower AC's that were attributed to their accumulation during the growth process.

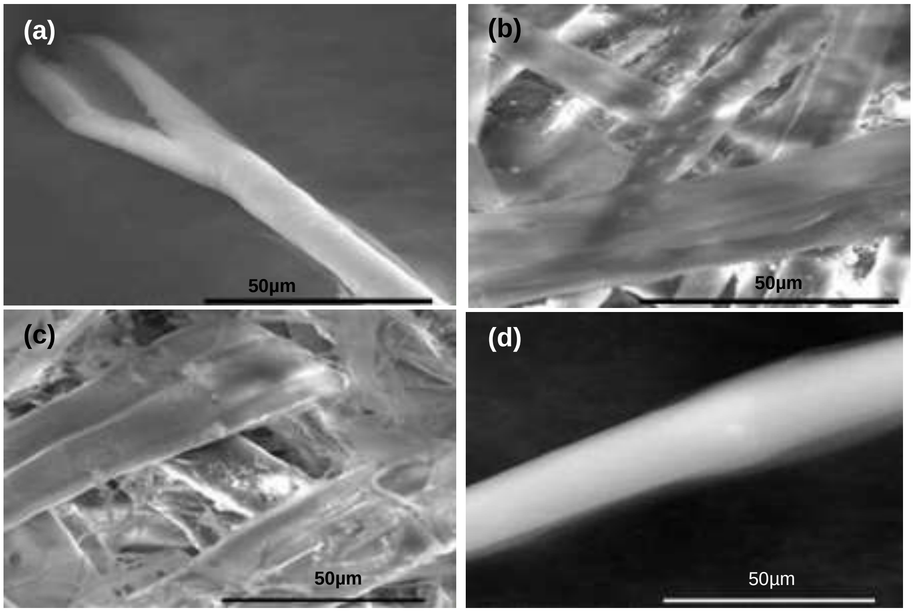

Fig. 1. Crude cellulosic resources: a) Cotton fibers, b) Recycled writing papers, c) Recycled newspapers, and d) Macerated woody fibers of *Leucaena leucocephala*

The presence of permeable structure in the cellulosic resources was very important for the chemical reagents penetration required for fiber swelling (*i.e.*, glacial acetic acid) and acetylation (*i.e.*, acetic anhydride). Sulfuric acid was used as a catalyst and was responsible for enhancing the acetylation efficiency. The mean values of PD for the crude cellulosic resources were estimated at 4.01, 3.6, and 2.4 µm for macerated woody fibers of *Leucaena leucocephala* (MWFL), RWP, and RNP, respectively (Fig. 1a,b,d). Furthermore, the diameter of a border pit torus in RNP (Fig. 2a) was found to be 3.6 µm while a natural crack width equals 20.6 µm (Fig 2a). Simple perforated plate of the leucaena vessel had a diameter of 40.5 µm (Fig. 2c). These openings, cavities, and the amorphous region within the cell wall microfibrils exhibit their own permeable structure for each cellulosic resource.

The acetylated product (AP) yields were 112, 94, 84, and 73% for cotton fibers (CF), recycled writing papers (RWP), recycled newspapers (RN), and macerated woody fibers of *Leucaena leucocephala* (MWFL), respectively (Table 3). In addition, for the same sequence of cellulosic resources, the same trend was observed for the yield of CTA. The highest yields of AP and CTA for CF can be attributed to the higher content of α-cellulose in these resources compared to the other cellulosic resources.

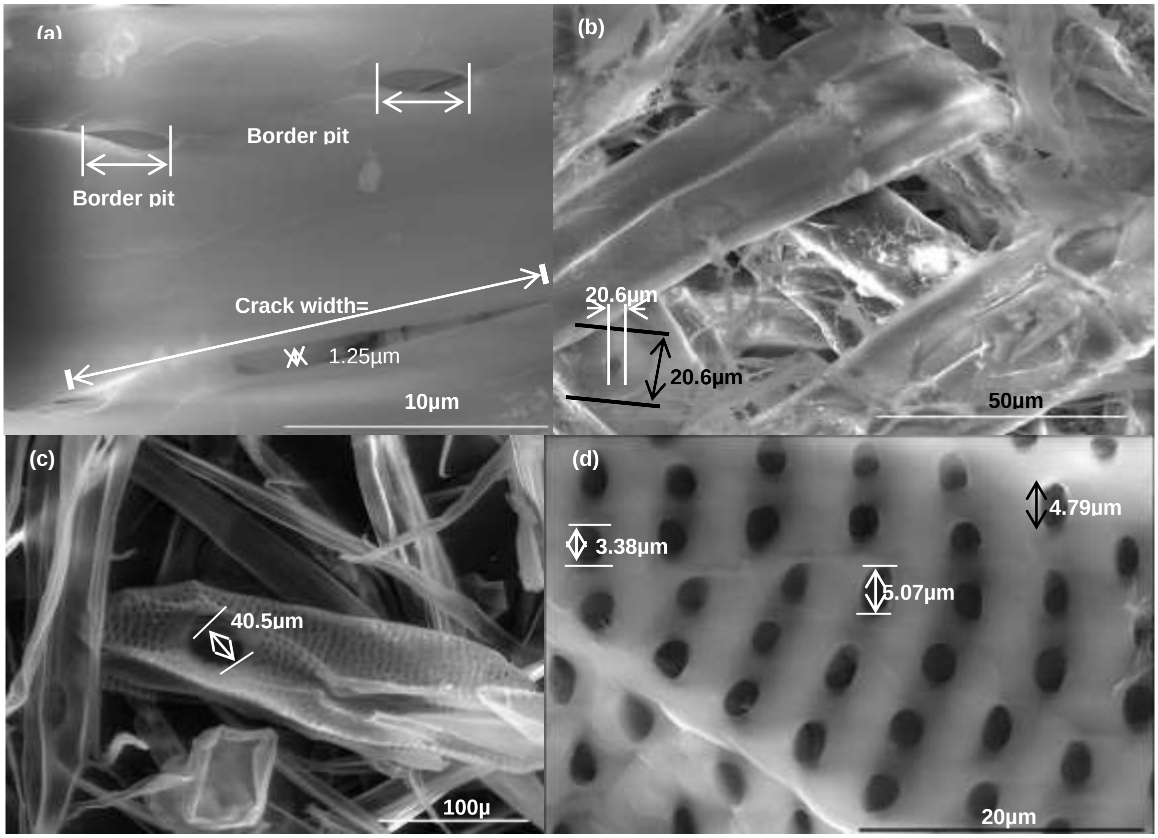

Fig. 2. Permeable structure of: a) recycled writing papers, b) recycled newspapers, c & d) vessel inner wall of *Leucaena leucocephala*

Table 3. Mean Values[1,2,3] of Acetylated Product (AP) and Cellulose Triacetates (CTA) Yields, Degree of Substitution (DS), and Pore Diameter (PD)

Cellulosic Precursors[4]	Yield (%)		DS	PD (nm)
	AP	CTA		
CF	112.18^{a}	87.08^{a}	2.86^{ab}	256^{a}
RWP	94.43^{b}	79.96^{b}	2.84^{c}	83^{d}
RN	84.37^{c}	68.17^{c}	2.85^{bc}	142^{b}
MWFL	72.98^{d}	54.63^{d}	2.89^{a}	108^{c}

[1] Means within the same column followed by the same letter are not significantly different according to LSD at $P < 0.05$
[2] Based on the oven-dry weight of purified cellulose
[3] Each value is an average of 12 samples
CF: cotton fibers; RWP: recycled writing papers; RN: recycled newspapers; MWFL: macerated woody fibers of *Leucaena leucocephala*

The results were comparable with the percentage of cellulose acetate (CA) obtained by Barkalow *et al.* (1989) who found that the weight gains at high yields of cellulose acetate were because of the addition of acetyl groups. This indicated that at high acid levels, the hemicellulose fraction was degraded and lost during processing, which reduced the yield. Accordingly, CF, RWP, and RN seemed to be more susceptible to acetylation than that of MWFL. However, the cellulosic resources appeared to be more significant in the production of CTA because of their higher yields. The differences in CTA yields were likely because of the differences in physical structure, especially regarding to porosity and crystallinity that affected the acetylation process.

Solubility Test

The solubility test for the resultant CA indicated that it was soluble in chloroform and insoluble acetone (Table 4). Since cellulose diacetate (CDA) dissolves in acetone and CTA dissolves in chloroform and a mixture of chloroform and methanol (9:1, v/v), the resultant material is CTA. By chemical modification done upon acetylation, approximately 80 to 92% of the hydroxyl groups on the cellulose chain were converted into acetate groups of cellulose di- and tri-acetate, respectively, as indicated by Israel *et al.* (2008). This finding confirms that rapid pouring of the acetylated liquor at the end of this process (30 min) in distilled water at about 25 °C did not hydrolyze the resultant CTA into CDA.

Table 4. Solubility Test for the CTA Samples[1] Produced from the Cellulosic Resources

Cellulosic Resources	Acetone	Chloroform	Chloroform and methanol mixture (9:1, v/v)
CF	insoluble	soluble	soluble
RWP	insoluble	soluble	soluble
RN	insoluble	soluble	soluble
MWFL	insoluble	soluble	soluble

[1] Each observation is a mean of 9 samples

CF: cotton fibers; RWP: recycled write papers; RN: recycled newspapers; MWFL: macerated woody fibers of *Leucaena leucocephala*

The formation of CTA and the DS were monitored *via* NMR spectroscopy. The DS was calculated using the integration of the ^{1}H-NMR resonances assigned to methyl groups and those of the hydrogen atoms bonded to the glucosidic groups. The ^{1}H-NMR spectra for the four cellulosic precursors are presented in Figs. 3 to 6. The NMR spectrum of the CTA was found to consist of two adsorption regions belonging to the substituted acetyl groups and protons of anhydroglucose unit (Goodlett *et al*. 1971). The first adsorption region was differentiated into three different peaks at 1.946, 2.012 and 2.132δ. In addition, the second adsorption region was found to be separated into seven peaks at chemical shifts ranged from 3.546 to 5.071δ (Fig. 3 to 6).

Table 3 lists the average DS at the individual 2, 3, and 6 hydroxyl positions of the glycosyl ring (DS_2, DS_3, and DS_6). Since those numbers are approximately the same, the reactivity of the individual hydroxyl groups towards acetylation was roughly the same under the conditions employed for this investigation. It can be seen from the results that the DS of the CTA from CF, RWP, RN, and MWFL were nearly identical (2.86, 2.84, 2.85, and 2.89, respectively), as shown in Table 3. These values offer additional confirmation, besides those from solubility test, that the products from the acetylation process are CTA with the chemical formula presented in Fig. 7.

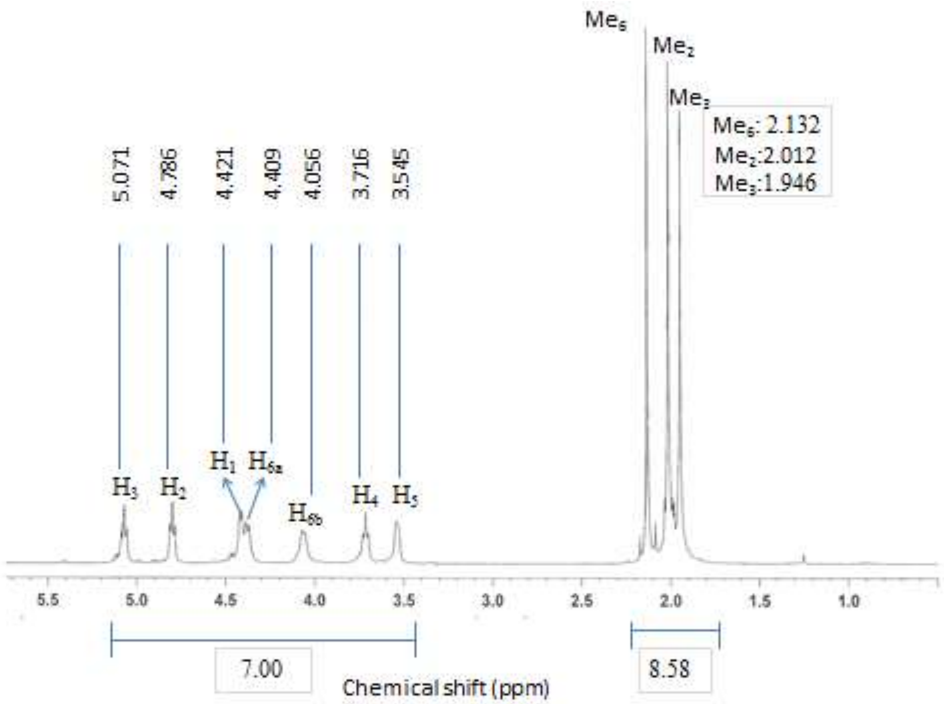

Fig. 3. ^{1}H-NMR spectrum of cellulose triacetate (DS = 2.86) produced from cotton fibers (CF). Me refers to methyl protons in acetyl group, H to protons on anhydroglucose, and subscripts to positions of Me or H on the anhydroglucose.

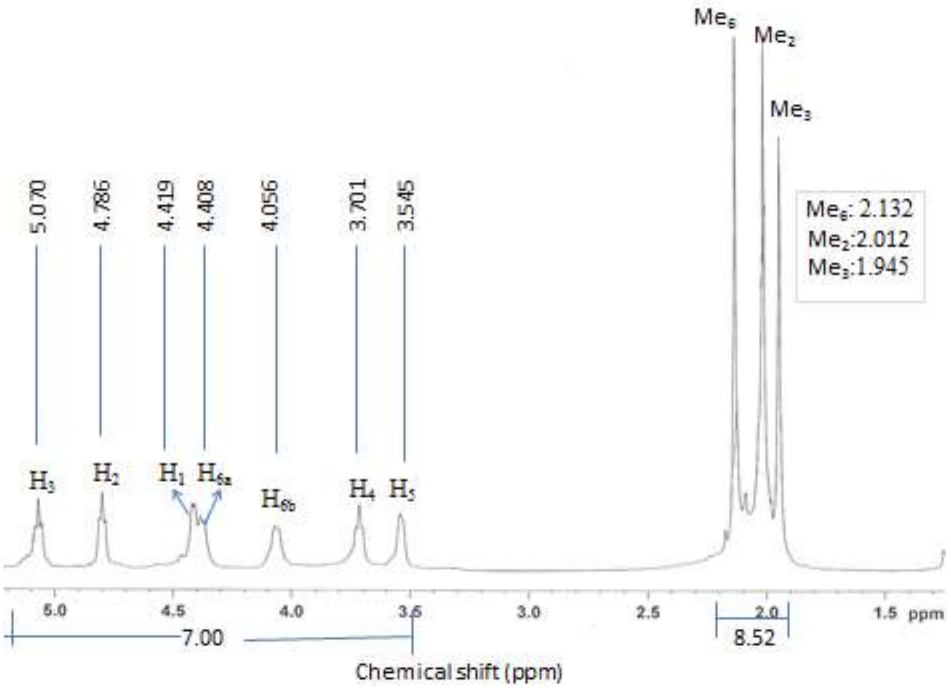

Fig. 4. ^{1}H-NMR spectrum of cellulose triacetate (DS = 2.84) produced from recycled writing papers (RWP). Me refers to methyl protons in acetyl group, H to protons on anhydroglucose, and subscripts to positions of Me or H on the anhydroglucose.

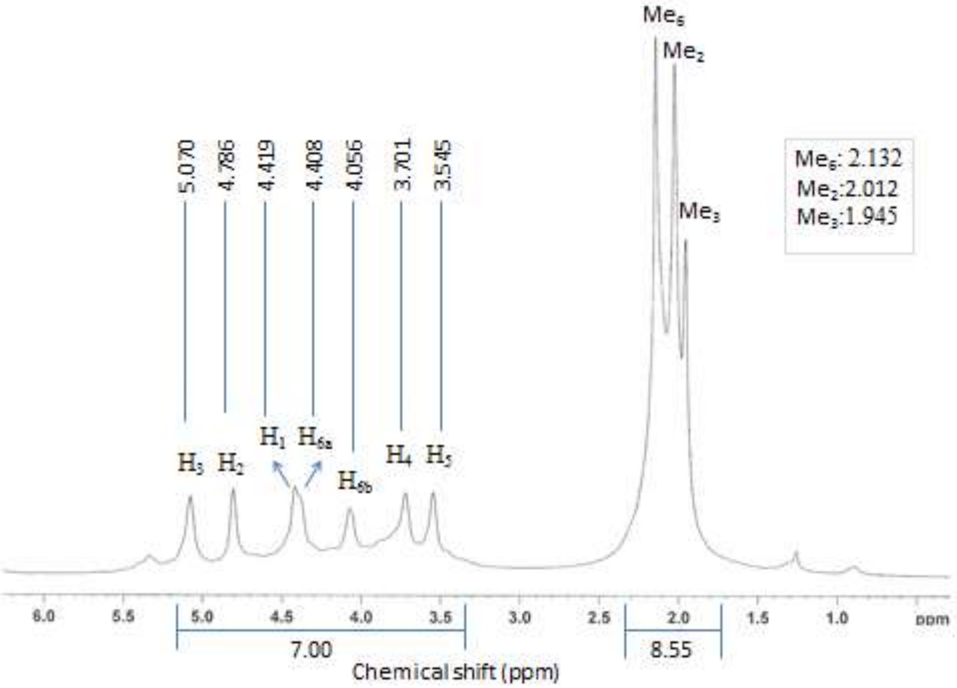

Fig. 5. ^{1}H-NMR spectrum of cellulose triacetate (DS = 2.85) produced from recycled newspapers (NP). Me refers to methyl protons in acetyl group, H to protons on anhydroglucose, and subscripts to positions of Me or H on the anhydroglucose.

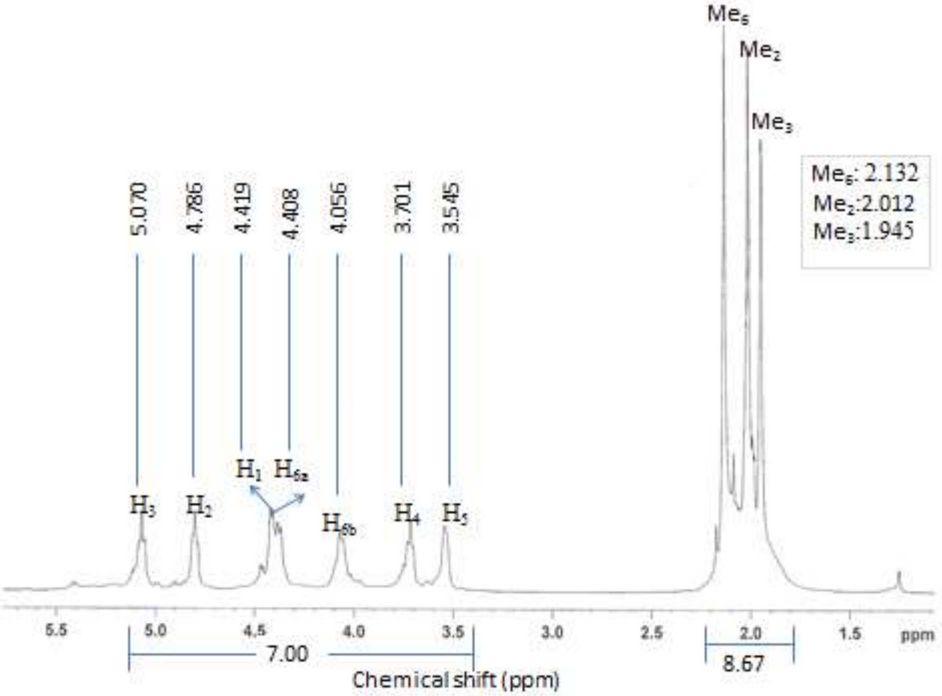

Fig. 6. ^{1}H-NMR spectrum of cellulose triacetate (DS = 2.89) produced from macerated woody fibers (MWFL) of *Leucaena leucocephala.* Me refers to methyl protons in acetyl group, H to protons on anhydroglucose, and subscripts to positions of Me or H on the anhydroglucose.

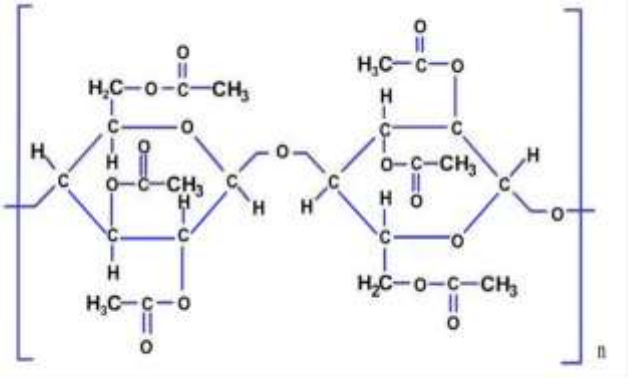

Fig. 7. Chemical formula of cellulose triacetate (CTA)

Morphological characterization of CTA can help in illustrating the influence of processing conditions on the reaction mechanisms, however it does contain a limited depth penetration in the field (Tang *et al.* 1997). For example, the surface of the CF is normally smooth (Fig. 2a), similar to other precursors; however, when acetylation proceeded at the reaction conditions used, the roughening of the surface texture together with the manifestation of the supermolecular structure of cellulose can be observed using SEM magnification of the CTA sample (Fig. 8).

The results are similar to those obtained by Israel *et al.* (2008), Cheng *et al.* (2010), Peres de Paula *et al.* (2008), Cao *et al.* (2007), and Ciacco *et al.* (2000). It can be seen in Table 3 that the PD of the CTA skeleton ranged from 0.072 to 0.239 μm for RWP and RNP, respectively. According to Tang *et al.* (1997), the dimensions of the pinholes were approximately 0.1 to 5-10 μm for CTA and more than 50 μm for CDA. These results confirm the presence of CTA. The SEM micrographs of the produced CTA are presented at Figs. 9 to 12.

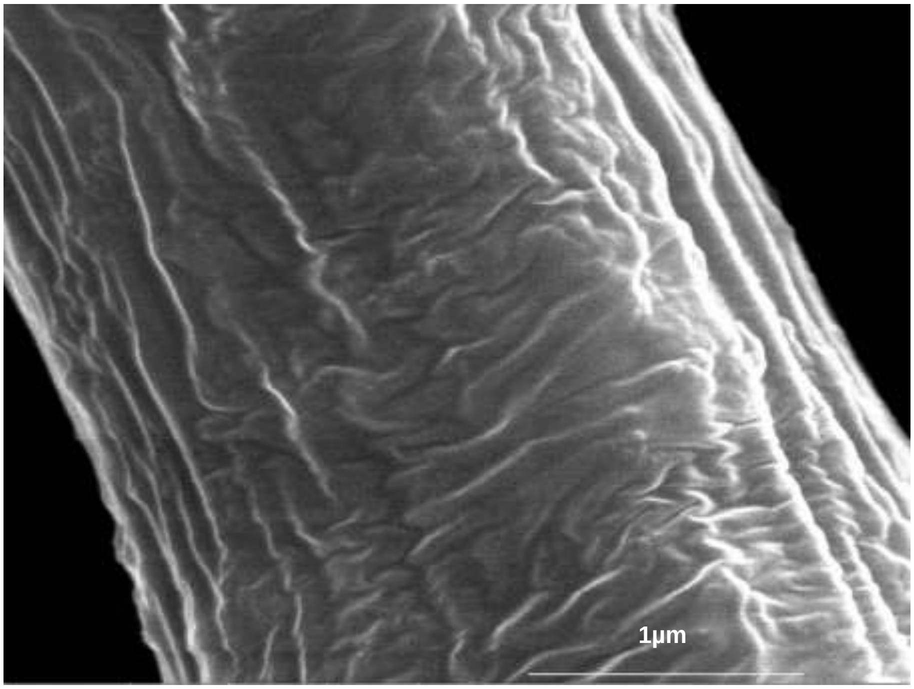

Fig. 8. Cotton fiber (CF) upon acetylation to form cellulose triacetate (CTA) (89,705X)

The narrow range of the DS (2.84 to 2.89) as shown in Table 3 and obtaining CTA from the four cellulosic resources reflects a similarity in ease of the acetylation, although showing differences regarding FL and FW (Table 1) and permeable structure (Fig. 2). This trend may be attributed to the efficiency of the chemical pretreatment step by using glacial acetic acid with continuous stirring in the aim of swelling the cellulosic fiber's walls. This process makes fibers similar in their accessibility of reagents upon the subsequent acetylation process by using acetic anhydride and sulfuric acid catalyst.

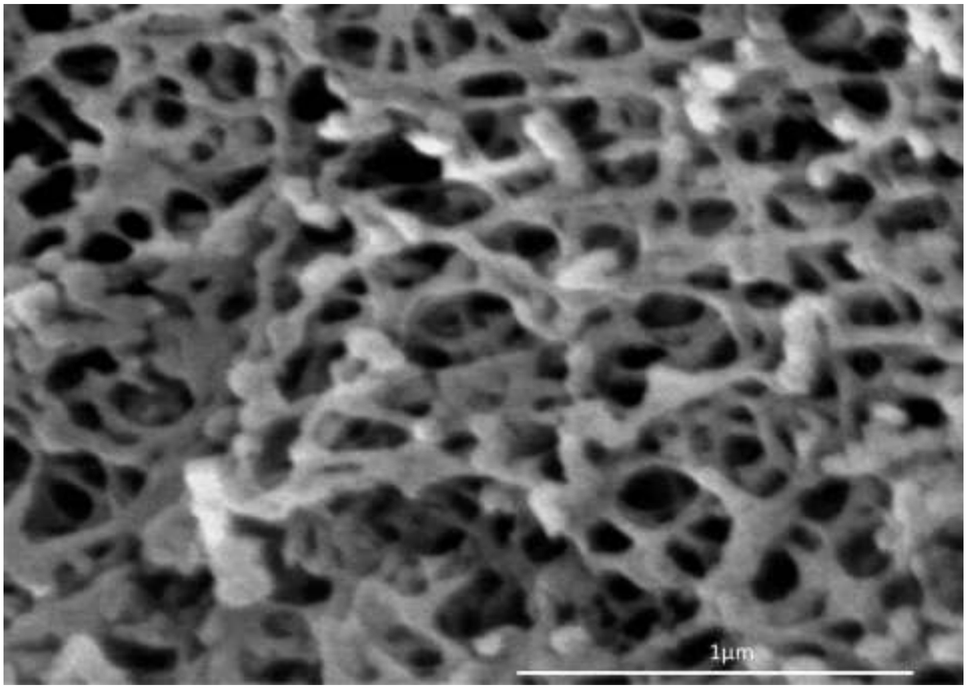

Fig. 9. SEM micrographs of cellulose triacetate produced from cotton fibers

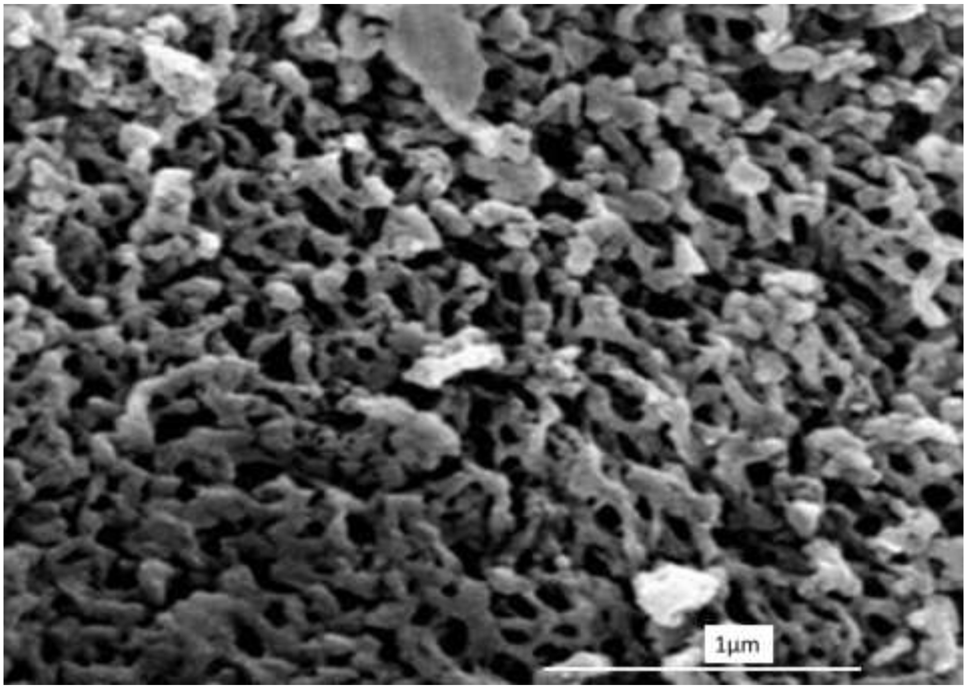

Fig. 10. SEM micrographs of cellulose triacetate produced from recycled writing papers

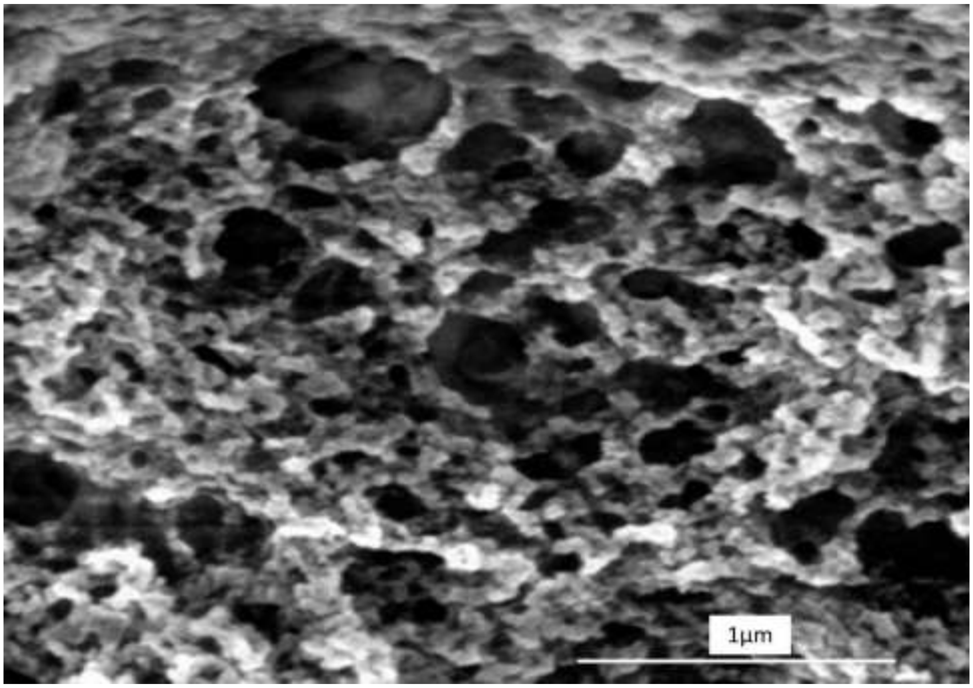

Fig. 11. SEM micrographs of cellulose triacetate produced from recycled newspapers

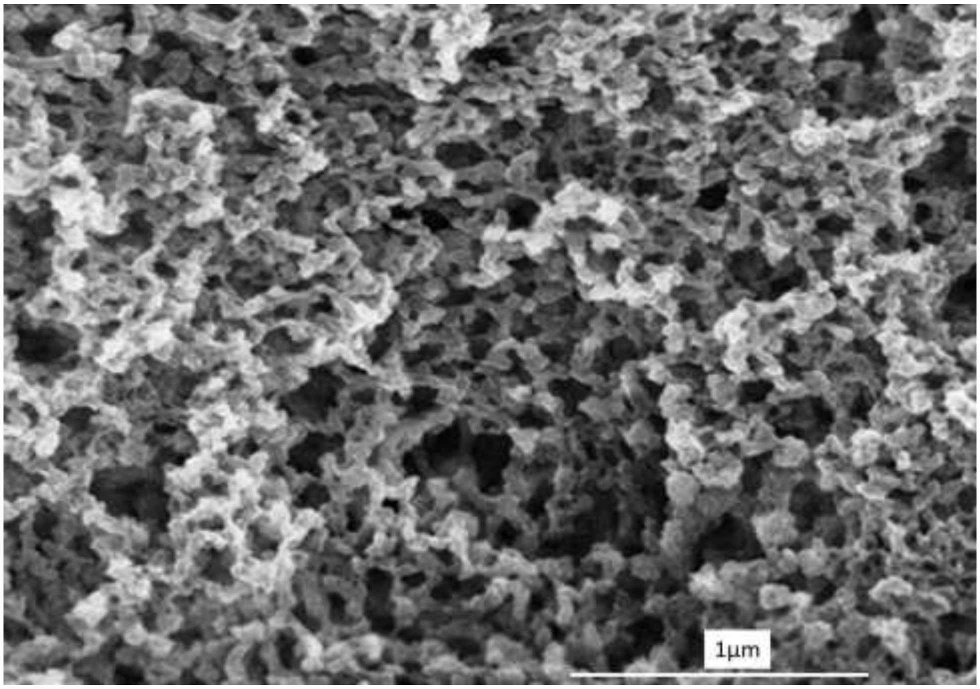

Fig. 12. SEM micrographs of cellulose triacetate produced from macerated woody fibers of *Leucaena leucocephala*

CONCLUSIONS

1. Purification of the parent cellulosic resource is an essential step to maximize the cellulose triacetate product.
2. The properties of the four cellulosic resources were significantly different. The cotton fibers had the highest length, while macerated woody fibers of leucaena had the smallest length and the greatest width.
3. The higher yield of each of the acetylated products and CTA was obtained from cotton fibers, recycled writing paper, and recycled newspaper. On the other hand, the macerated woody fibers of leucaena gave the lowest yield.
4. The acetylated cellulose was found to be soluble in chloroform and a mixture of chloroform and methanol (9:1v/v) and insoluble in acetone. These findings confirm the presence of CTA.
5. The NMR spectrum of the CTA consisted of two obvious adsorption regions. The 1st region belongs to the substituted acetyl groups and was differentiated into three different peaks at 1.946, 2.012, and 2.132δ. The 2nd region corresponds to protons of anhydroglucose units and was separated into seven peaks at chemical shifts ranged from 3.546 to 5.071δ
6. The DS values of the four CTA's were similar and could offers additional confirmation beside the solubility test to the presence of the CTA. The PD value of the CTA skeleton is within the known scale of CTA pinholes and was much lower than that for CDA, which confirmed the presence of CTA.

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