



Autoclave and ultra-sonication treatments of oil palm empty fruit bunch fibers for cellulose extraction and its polypropylene composite properties



M.A. Abdullah ^{a,*}, M.S. Nazir ^{b,1}, M.R. Raza ^c, B.A. Wahjoedi ^d, A.W. Yussof ^e

^a Institute of Marine Biotechnology, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia

^b Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

^c Department of Mechanical Engineering, COMSATS Institute of Information Technology, Lahore 57000, Punjab, Pakistan

^d Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia

^e FELCRA Nasaruddin, Oil Palm Mill, KM37, JalanTronoh, 32600 Bota, Perak, Malaysia

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ABSTRACT

Accumulation of residual plastics and the biomass wastes from agricultural sectors are causing serious global environmental problems if not addressed effectively. Cellulose with polypropylene as bio-composite material is an elegant strategy for value-added utilization of wastes. In this study, green isolation of cellulose from oil palm empty fruit bunches by autoclave-based and ultrasonication pre-treatments were developed to replace the non-green chlorite method. Ultrasonic treatment with hydrogen peroxide yielded 49% cellulose with 91.3% α -cellulose content and 68.7% crystallinity, as compared to 64% cellulose with autoclave treatment. Based on field emission scanning electron microscope, the ultrasonic and the autoclave-treated fibers showed complete separation of cellulose fibrils, with punctures and pores on the surface. High resolution transmission electron microscope and X-ray diffraction studies suggested monoclinic unitary crystal structure. The cellulose/polypropylene composite fabrications were achieved by using injection-molding technique where the composites with 25% cellulose loading gave high tensile strength of 27 MPa, without any addition of coupling agents. Thermogravimetric analysis study showed that the thermal stability of composites was enhanced by 150 °C as compared to singular cellulose and polypropylene. The low water and diesel uptake suggested the compact structure of the composites. This study has developed green techniques combining heat and eco-friendly chemical treatment for cellulose extraction from agro-lignocellulosic wastes. The cellulose/polypropylene composites developed with high tensile strength, high thermal stability, and low water and diesel sorption have great potentials for conversion into eco-composite products such as polymeric material insulated cables for high voltage engineering, automotive parts, sports tools and other household or office items.

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1. Introduction

The total world biomass production of lignocellulosic material including herbaceous and woody crops is approximately 10 Mg ha⁻¹ per year, with the temperate and sub-tropical rain forests contributing approximately 8–22 Mg ha⁻¹ per year (Perlack

et al., 2005). Lignocellulose is compact with cellulose as the backbone, having parallel rod-like structure along with the deposition of hemicellulose and lignin. The crystalline and amorphous region depends on the laterally stable arrangement of cellulose molecules through H-bonding of cellulose-OH...OH-cellulose (Klemm et al., 2005; Rowell et al., 2005). The more high valued lignocellulosic fractions as cheaper sources for biorefineries are celluloses and hemicelluloses but lignin has also found diverse applications (Lora and Glasser, 2002). The special properties of cellulose such as hydrophilicity, chirality, capacity for broad chemical modification, and the formation of versatile semicrystalline fiber morphologies (Klemm et al., 2005; Zhu et al., 2006), are suitable characteristics

* Corresponding author. Tel.: +609 6683104/3661; fax: +609 6683105.

E-mail addresses: joule1602@gmail.com, azmuddin@umt.edu.my (M.A. Abdullah).

¹ Present address: Chemical Engineering Department, COMSATS Institute of Information Technology, Lahore 54000, Punjab, Pakistan.

for applications in pharmaceutical, cosmetic and stabilizer purposes.

Microcrystalline cellulose (MCC) is a biodegradable, insoluble, and white color biopolymer which can be extracted from lower plants such as bacteria, algae and fungi and higher woody plants. MCC has very good extruding property for which it is recommended for various polymer composites preparations (Chuayjuljit et al., 2010). Several types of lignocellulosic fibers blended with chemicals such as starch, polylactic acid (PLA), poly-hydroxyl alkanooates (PHA) and poly-hydroxyl butyrates (PHB) and polyolefin and polypropylene composites have been reported (Yu, 2009; Malkapuram et al., 2009) using fabrication techniques such as compression and injection molding. Composites of softwood cellulose pulp fibers and Doum fibers with virgin low density polyethylene (LDPE) have been prepared by batch melt mixing or twin-screw extrusion achieving the tensile modulus and strength in the range of 0.25–0.48 GPa and 10–11 MPa, respectively (Sdrobis et al., 2012; Arrakhiz et al., 2013). In the automotive industry, natural fiber composites are used because of easy and cost-efficient processing of materials with a resilient formula and long know-how, weight reduction (up to 30%), price competitiveness, good accident behavior, good mechanical and acoustic properties, low fogging, no cracking on contact, flame resistant and high bio-based share (Dammer et al., 2013).

The total cellulose production is 10^{11} – 10^{12} t per year (Yuan et al., 2010), and is annually consumed at 7.5×10^{10} t (Jacqueline and Kroschwitz, 2001). The sources of cellulose should be ideally from economical, easily accessible agro-wastes. Oil palm biomass, for example, constitutes 85.5% of generated wastes in Malaysia, which includes fruit pulp, oil palm empty fruit bunch (EFB), kernel and shell (Goh et al., 2010). EFB singularly generates 19.8 million tonnes of biomass annually on wet basis (Ng et al., 2011). Lignocellulosic EFB fibers, composed of 444 g kg^{-1} cellulose content, can be transformed into value-added biopolymer (Rosnah et al., 2009) such as for bioethanol production, paper and fiber board manufacturing, or developed into green fertilizer. As raw EFB is a composite with compact fibrillar packing and irregular heavy deposition of wax, hemicelluloses, lignin, and inorganic components (Na, Mg, K, Ca, S, Al, Si) (Nazir et al., 2013), extraction of cellulose requires the opening and breaking of chemical bonding such as the aromatic –OH, C–C, R–O–R of the lignins and the H-bond RCOOR and R–O–R of the hemicelluloses or celluloses. Cellulose separation can be achieved by dislocating the packed composite structure, by breaking the H- bonding.

The chlorite (ClO_2^-) method for delignification and extraction of cellulose from wood materials involves the use of acidified sodium chlorite ($\text{NaClO}_2 + \text{H}_3\text{O}^+$) (Wise et al., 1946) which generates chlorine free radical, Cl^\cdot , and highly toxic organochlorine compounds. The extraction of MCC from EFB using chlorite method has been reported (Rosnah et al., 2009). Ultrasonic-assisted alkali extraction as chlorine free extraction of cellulose and delignification has been studied on wheat straw (Sun et al., 2004) and barley straw (Sun et al., 2005), and on EFB with sulfuric acid hydrolysis (Fahma et al., 2010). We have reported the use of eco-friendly reagents with 20% (v/v) formic acid and 10% (v/v) hydrogen peroxide employed at 85°C , and the autoclave treatment for cellulose extraction from the EFB. The yield of 64% (w/w) achieved with α -cellulose content of 93.7% and 69.9% crystallinity was among the highest ever being reported (Nazir et al., 2013).

In the present work, green pre-treatment method was employed by using synergistic effects of low concentrations of NaOH and hydrogen peroxide and ultrasonic treatment of 40 kHz frequency with 100% amplitude at room temperature to extract cellulose from EFB. Comparison of the morphological, chemical and thermal characteristics of the purely extracted cellulose (PEC) was

made with the PECs from the autoclave treatment and the commercial MCC. The effects of pre-treatment methods and PECs loading on the mechanical properties, the morphological, thermal, water and diesel sorption characteristics of the cellulose/PP composites were then investigated.

2. Materials and methods

2.1. Materials

EFB samples were collected from FELCRA Nasaruddin Oil Palm Mill Sdn. Bhd., Bota, Perak, Malaysia. The chemicals such as ethanol (ACS Reagent, Merck), sodium hydroxide (Pellet), 30% hydrogen peroxide (R&M Chemicals), were used as purchased. Commercial MCC powder of $20 \mu\text{m}$ particle size was obtained from Sigma–Aldrich (USA). Instruments used were sonicator at 40 kHz (Elma Transsonic T910 DH) and the autoclave ($75\times$, All American).

2.2. Sample preparation

EFB fibers were physically separated into long fibers and suspended in 1% detergent to remove oil, greases and suspended particles. Clean fibers were dried in an oven at 100°C for 12–24 h until constant weight and the moisture content was determined according to ASTM-D4442-92 standard. Fibers were cut into 0.2 mm length by using power cutting mill (PULVERISSETTE 25), and dewaxed by reflux with ethanol in Soxhlet apparatus for 6 h, followed by thorough washing with deionized water. A portion of fibers were kept in a desiccator and used for raw EFB characterization.

2.3. Pre-treatment methods

The ultrasonic treatment (SONO-CHEM) method was adopted as reported before (Sun et al., 2004; Fahma et al., 2010) but modified accordingly for EFB. Oil free EFB fibers were suspended in 250 ml of 2% NaOH, shaken for 30 min at 250 rpm, followed by the addition of 250 ml of 10% (v/v) of 30% H_2O_2 . The beaker containing suspended fibers was sonicated at 40 kHz for 1, 2 and 3 h at room temperature. The fibers were collected by vacuum filtration, washed with deionized water, the residue dried in an oven at 100°C for 12 h and weighed. The light yellow color fibers from ultrasonic treatment were further treated with 100 mL L^{-1} H_2O_2 at pH 11 for 90 min to obtain white fibers. The white insoluble fibers were filtered and washed with deionized water. Cellulose fibers were collected and yield was calculated on the weight basis (w/w). The α -cellulose content was calculated by TAPPI standard method (TAPPI, 1991).

The autoclave treatment (AUTO-CHEM) method was as reported before (Nazir et al., 2013).

2.4. Characterization

Microscopic structure and elemental analysis of raw EFB and PECs were determined by using FESEM (Zeiss Supra 55VP) and EDX analysis. High resolution TEM (TEM, Libra 200 FE, ZEISS) was used to study the underneath layers of sample structure and evaluate the diffraction pattern of cellulose. Diffraction of sample was analyzed by using software (ITEM, Olympus) equipped with TEM by Fast Fourier Transmission method.

The molecular weight and degree of polymerization (DP) of PEC and the commercial MCC were determined by using gel permeation chromatography (GPC) technique. The samples were analyzed by TSK gel Super AWM-H $\times 2$ column and dimethylacetamide (DMAc) containing 0.5% of LiCl as eluent. Sample was pretreated by dissolution in DMAc containing 8% of LiCl at 40°C for 2 days. Sample was

further diluted to 0.5 g L⁻¹ and eluted with the run time set for 45 min (Strlič and Kolar, 2003; Catherineh et al., 2009).

DP was determined by dividing the average molecular weight (M_w) by the unit formula weight of cellulose monomer unit anhydroglucose (C₆H₁₀O₅) which possesses one less water molecule as compared to glucose, and the formula weight was 162 g mol⁻¹. DP provides the information about the number of monomer units present in the polymeric cellulose chain.

Functional group changes of samples were scanned at the range of 4000–450 cm⁻¹ by using FTIR (Spectrum One, Perkin–Elmer).

Crystallinity of PECs was investigated using X-ray diffraction (D8-Advance Bruker-AXS). Samples were tightly packed in crucible and analyzed at 2 θ scan at wide angle range of 2–80°, with step width of 2° per second at 25 °C. The crystallinity of samples was calculated as reported previously (Segal et al., 1959).

The thermal stability and degradation with respect to mass losses of PEC in an inert nitrogen environment were investigated using thermogravimetric analysis (Pyris 1, Perkin Elmer) at 30–700 °C with a scan rate of 10 °C per minute.

2.5. Cellulose/PP composite

The raw EFB fibers were suspended in 150 mL ethanol and NaOH solutions, treated under Soxhlet for 6 h to dewax, filtered and washed with deionized water to remove any traces. The fibers were dried further in an oven at 100 °C for 12 h and used for composite preparation.

The Soxhlet-treated fibers, and the fibers from SONO-CHEM and AUTO-CHEM methods, were fabricated into composites with PP. These are classified as raw EFB (raw), purely extracted cellulose by SONO-CHEM (PEC-US), purely extracted cellulose by AUTO-CHEM (PEC-AUTO), Raw EFB/PP (raw/PP), Ethanol-treated/PP (EtOH/PP), NaOH-treated/PP (NaOH/PP), PEC-US/PP and PEC-AUTO/PP composites.

The treated fibers were blended with PP in an internal mixer machine (ThermoPolylab, HAAKE, Germany). PP was melted in the internal mixer at 170 °C and 120 rpm, followed by multiple small additions of fibers to avoid agglomerates and left to stand under the same conditions for 30 min to ensure homogeneity. The uniformly mixed composites stuck to the blades were removed by an iron scrubber.

Compact lumps of composites were converted into small granules by using power cutting mill (PULVERISSETTE 25). All fiber/PP composites were fabricated by using vertical injection molding machine (Semi-automatic, KSA100). The composites were filled into a hopper, leading to the thermocouple barrel where they were melted at 170 °C. The mold was placed and screwed at the end of the injection barrel head, onto the support base. The mold was layered with releasing agent to make it easy to take the fabricated composite out without cracks. The auto-injection filling time depends on the viscosity of the composite and the mold size. The fabrication duration was set for 5 s. After the required filling, the mold was allowed to cool and then unscrewed to get the fabricated composite. The standard fabricated dumb-bell shape composite and its dimensions (25 mm length \times 5.91 mm width \times 3.19 mm thickness) are shown in Fig. 1 a and b.



Fig. 1. Standard test specimen: (a) fabricated composite, (b) the dimension.

Ten samples were prepared from each composition with 10% PEC loading of raw/PP, EtOH/PP, NaOH/PP, PEC-US/PP and PEC-AUTO/PP. These were further fabricated with 10%, 20%, 25% and 30% PEC loading. With standard dimensions, any higher loading may limit the composite fabrication in PP. The mechanical, morphological and thermal properties were investigated.

2.6. Properties

2.6.1. Mechanical

The tensile properties of the composite samples were determined by Universal Tensile Machine (UTM) LR-5K (Lloyd Instrument Ltd U.K) according to ASTM D 638-03 standard. The cross head speed of the sample holder was set at 1 mm min⁻¹. The cumulative average of the tested samples was recorded for each composite.

2.6.2. Thermogravimetric analysis (TGA)

The thermal stability of the raw EFB, cellulose and the PP composites was investigated by using the TGA (Pyris 1, Perkin Elmer). The sample was heated from 50 to 700 °C with heating rate of 10 °C min⁻¹ in continuous nitrogen flow of 20 mL min⁻¹.

2.6.3. Water absorption

The weight of the samples was measured before and after the treatment. The samples were carefully cut in a liquid nitrogen environment to avoid fractures and cracks. The oven dried samples of similar sizes were immersed in water for a month and the water absorption was noted after every five days. The percentage of the water absorption was determined as follows:

$$\text{Water absorption(\%)} = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

where W_0 (g) is the weight of the oven dried composite, and W_1 (g) is the weight after water immersion.

2.6.4. Diesel sorption

After tensile test, the remaining parts of the samples were tested for oil sorption according to F 726-99 method (ASTM, 1998). Approximately 1 g of sample was dipped in 400 mL of diesel in 500 mL glass beaker. Test sample was drawn out after 30 min and left hanging at the top of oil beaker. The dripping of oil was noted. Oil sorption capacity and the percentage of dynamic oil retention were calculated as follows:

$$\text{Oil sorption capacity (g/g)} = \frac{SA - SF}{SD} \quad (2)$$

where SA, weight of oil in the beaker before adsorption (g); SF, weight of oil after 1 min dripping (g), SD, weight of dry sample (g).

$$\text{Dynamic oil retention(\%)} = \frac{W_t}{W_t = 1} \times 100 \quad (3)$$

where $W_t = 1$, weight of oil beaker at 1 min dripping; W_t , weight of oil in beaker at $t = 2, 3, 4, 5 \dots 30$ min.

3. Results and discussion

3.1. Cellulose extraction

The moisture content of raw EFB fibers was 9.9% as determined by ASTM-D 4442-92 standard, which was comparable to 10.6% reported previously (Ahmad et al., 2007). As shown in Table 1, based on GPC analyses, the M_w of SONO-CHEM PECs of

$1.49 \times 10^5 \text{ g mol}^{-1}$ was comparable to commercial MCC of $1.48 \times 10^5 \text{ g mol}^{-1}$, but that of AUTO-CHEM PECs were much higher at $1.87 \times 10^5 \text{ g mol}^{-1}$. The DP of SONO-CHEM PECs and commercial MCC were 919 and 913, respectively, but the AUTO-CHEM PECs was 1154. The α -cellulose content achieved with SONO-CHEM treatment was 91.3%, while with AUTO-CHEM treatment was 93.7%. The 2 h SONO-CHEM was proven effective for cellulose extraction at 490 g kg^{-1} yield, higher than the reported values using chlorite method (Rosnah et al., 2009), and it adequately changes the EFB mechanical properties, and the cavitations enhance the mass transfer (Yunus et al., 2010). Cavitations produced under ultrasonic irradiation with high energy and high temperature, may be sufficient to loosen the hard texture of the EFB, assists the penetration of H_2O_2 , and synergistically dislocate the tight coupling of lignocellulosic fiber, breaking the specific oriented layer (Mason et al., 1996). However, the 1 h SONO-CHEM treatment is insufficient leading to partial penetration of H_2O_2 while the 3 h treatment may be too long to cause depolymerization of cellulose layer as well. Hydrolysis and depolymerization of lignin could release the celluloses due to the presence of lignin covalent bond and the weak hemicelluloses–cellulose H-bonding in lignocelluloses (Faulon et al., 1994). Infact, the energy required to cleave the H-bond in cellulose at $8\text{--}15 \text{ kJ mol}^{-1}$ is even lesser than to break H-bonding in water molecule at $18\text{--}21 \text{ kJ mol}^{-1}$ (Bochek, 2003).

The effectiveness of the combined heat and chemical treatment has been further proven by a new method combining steam flash-explosion and alkaline treatment (SFE-AT) to extract cellulose fibers from the bark of cotton stalks with 79.6% cellulose content (Hou et al., 2014). Our AUTO-CHEM method is also superior in achieving higher yield of 64% cellulose yield (Nazir et al., 2013) as compared to the formic acid/peroxyformic acid/hydrogen peroxide process on jute fiber which only achieves 59.8% yield (Jahan et al., 2011). The autoclave pretreatment at $121 \text{ }^\circ\text{C}$ and 15 psi with different chemicals for different durations, not only disinfects but also disassemble the lignocelluloses and opens up for the penetration of reagents and for hydrolysis to take place for higher cellulose yield (Nazir, 2013).

3.2. Morphological characterization

The FESEM micrograph suggests that raw EFB (Fig. 2a–c) has tight packing of hemicellulose/cellulose and lignin in composite structure embedded with inorganic particles. The EDX analyses (Table 2) suggest low percentage of carbon and oxygen with high inorganic elements such as sodium, magnesium, aluminum, sulfur, potassium and calcium, with silica deposition relatively high at 4.61%. The tight packing is due to the presence of H-bond between cellulose/hemicellulose/lignin and forms a highly ordered structure. The combined strength of H-bond of 25 kJ mol^{-1} , covalent O–H bond of 460 kJ mol^{-1} and Van der Waal's interaction of 0.15 kJ mol^{-1} are responsible for the compactness of the fibril composite (Martins et al., 2011). The compact fibrillar arrangement also makes it difficult to segregate raw EFB into solitary fibers where the silica particles give extra resistance for hydrolysis of EFB

lignocellulose (Ghazali et al., 2009). The SONO-CHEM (Fig. 2d–f) and AUTO-CHEM-treated fibers (Fig. 2g and h) on the other hand, show complete separation of cellulose fibril from EFB composite. The inorganic particles removed can be observed as a scar on the surface (Fig. 2d and e) attributable to the sputtering of silica (Hamzah et al., 2011).

3.3. Chemical characterization

The FTIR spectra (Fig. 3) showed the transmittance peaks at 3400 cm^{-1} and 2906 cm^{-1} attributable to cellulose–OH and C–H group stretching vibration, respectively (Li et al., 2012) of raw EFB and PECs. The cellulose–water absorption peak at 1644 cm^{-1} and the peak 895 cm^{-1} assigned to β -glycosidic linkage (Mandal and Chakrabarty, 2011; Bian et al., 2012) are present in all spectra. However, the peak at 1735 cm^{-1} attributable to waxy C=O acetyl group or hemicelluloses ester or carbonyl ester of *p*-coumaric monomeric lignin unit, and the peak at 1248 cm^{-1} due to C–O–C of aryl-alkyl ether in lignin (Li et al., 2012; Nazir et al., 2013), are not present in the SONO-CHEM-PEC, AUTO-CHEM-PEC and commercial MCC. Similarly the peaks at 1432 cm^{-1} , 1375 cm^{-1} and 1326 cm^{-1} associated with bending vibration of $-\text{CH}_2$, C–H and C–O of hemicelluloses, and the peaks at 1165 cm^{-1} and 1037 cm^{-1} attributed to the deformation of CH-aromatic stretch of lignin and xylopyranose stretch, respectively (Jahan et al., 2011), are absent in PECs and commercial MCC. These suggest the removal of hemicelluloses and lignin from the PECs and the commercial MCC.

The amorphous and crystalline properties of sample were further proven by the XRD spectra of commercial MCC (Fig. 4a), AUTO-CHEM-PEC (Fig. 4b), SONO-CHEM-PEC (Fig. 4c) and raw EFB (Fig. 4d). The high intensity peak characteristic of cellulose was observed in all diffraction patterns at 2θ value of 22.5° as similarly reported earlier at $19\text{--}23^\circ$ (Lejeune and Deprez, 2010; Mohamad Haafiz et al., 2013), suggesting the presence of crystalline cellulose. The crystallinity index of raw EFB was calculated as 43.87% and the crystallite size was 31.5 nm, with high intensity peak (I_{002}) at 22.5° corresponding to crystalline region, and low intensity peak (I_{am}) at 15° corresponding to amorphous region. The SONO-CHEM-PEC and AUTO-CHEM-PEC crystallinity indices were calculated as 68.7% and 70%, respectively, comparable to Joint Committee on Power Diffraction Standard (JCPDS 03-0289) and the commercial MCC.

The high resolution TEM (micrographs not shown) suggests the presence of large crystalline region with different crystallite sizes and small amount of amorphous region. The differences between raw and treated PECs further support our postulation that the non-crystalline region was dissolved, leaving the crystalline region intact. To investigate the crystalline structure, TEM micrographs of PECs were analyzed by using ITEM (Olympus) software equipped with LIBRA (200FE). One part of live image was selected and cropped for FFT (Fast Fourier Transmission) where crystalline arrangement of cellulose can be observed. The diffraction patterns of SONO-CHEM and AUTO-CHEM cropped region were recorded and the interplanar distances were calculated, which suggest the equivalence to monoclinic crystal system. In unit cell monoclinic structure, all lengths must be different ($a \neq b \neq c$). The images show only $\alpha = \gamma (\approx 90^\circ)$, $\beta \neq 90^\circ$ angles (Nazir et al., 2013). The cellulose chain stability can be attributed to the Van der Waal's and H-bonding. The crystallinity indices of 68.7% and 74.9% reported for cellulose extracted from jute, respectively, use more acidic 2 N sulfuric acid at $100 \text{ }^\circ\text{C}$ for 2 h and 64% w/w sulfuric acid solution with elaborate procedures (Jahan et al., 2011). High crystallinity index of 87% for cellulose-I MCC from EFB can be achieved, but requiring the use of elaborate serial bleaching of oxygen-ozone and H_2O_2 before hydrolysis with 2.5 N HCl at $105 \text{ }^\circ\text{C}$ for 30 min with

Table 1
Physical properties of purely-extracted cellulose from empty fruit bunch.

Properties	SONO-CHEM-PEC	AUTO-CHEM-PEC
Moisture (%)	9.9	9.89
α -Cellulose (%)	91.3	93.7
Particle size (μm)	21.48	21.72
Density (g cm^3)	1.58	1.59
Molecular weight (g mol^{-1})	1.49×10^5	1.87×10^5
Degree of polymerization	919	1154

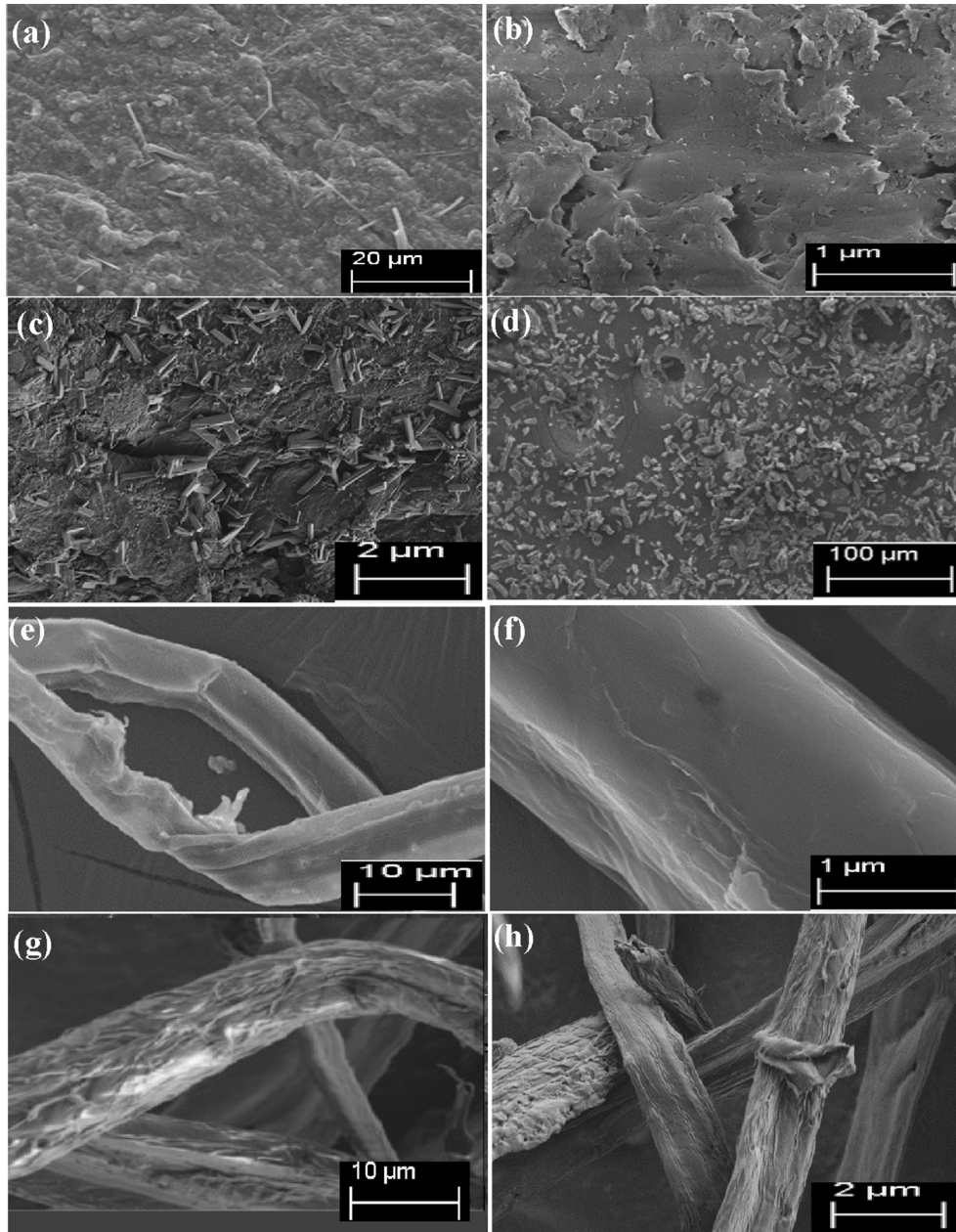


Fig. 2. Field emission scanning electron microscope micrograph of (a–c) raw empty fruit bunch, (d–f) ultra-sonicated purely-extracted cellulose (g,h) autoclave-based purely-extracted cellulose (Nazir et al., 2013).

Table 2
Elemental composition of raw empty fruit bunch and purely-extracted cellulose.

Element	Raw EFB		SONO-CHEM		AUTO-CHEM	
	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	44.79	54.31	66.34	72.42	63.16	69.54
O	44.41	40.43	33.66	27.58	36.84	30.46
Al	0.49	0.27	–	–	–	–
Ca	1.50	0.54	–	–	–	–
K	1.86	0.69	–	–	–	–
Mg	0.82	0.49	–	–	–	–
Na	1.00	0.64	–	–	–	–
S	0.52	0.24	–	–	–	–
Si	4.61	2.39	–	–	–	–
Total	100.00		100.00		100.00	

constant agitation at 1:20 ratio of pulp to liquor (Mohamad Haafiz et al., 2013). The higher or lower crystallinity will determine the intended use of final composite products.

3.4. PEC/PP composite

3.4.1. Effects of pre-treatment methods and 10% PEC loading

The pre-treatment of EFB fibers with EtOH and NaOH in Soxhlet apparatus showed partial removal of hemicelluloses and the wax coating, leading to partially exposed fibrils. The raw EFB, and the 10% (w/w) PECs from different pre-treatment methods were then blended and thoroughly mixed with PP for composite fabrication. Fig. 5a and b shows the stress–strain profile and Table 3 shows the mechanical properties, tensile strength, Young's modulus and elongation at break of the composites. The Young's modulus

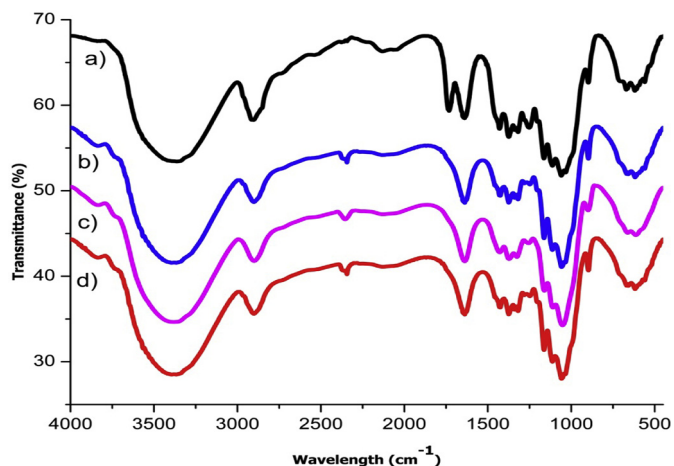


Fig. 3. Fourier transform infra-red spectra of (a) raw empty fruit bunch, (b) ultra-sonicated purely-extracted cellulose, (c) commercial microcrystalline cellulose, (d) autoclave-based purely-extracted cellulose (Nazir et al., 2013).

describes the material nature, either stiff or elastic, calculated based on a stress/strain graph in the linear region (elastic region). The composite with higher Young's modulus is categorized as stiff material whose shape changes very little under elastic load, whilst the lower Young's modulus material shows considerable change in shape. Elasticity of the lower Young's modulus should result in flexible properties for easy shaping without cracks. Elongation at break, calculated automatically from the computer software, describes the extent of strain in the composites.

The tensile strength of PP are reported to be 20 and 28.5 MPa (Stark and Rowlands, 2003; Slaughter, 2004). The reduced tensile strength at 10% PEC loading could be due to the compact PP matrix structure loosened up by the pores and the cracks with the presence of fibers (Stark and Rowlands, 2003). At 170 °C, the mixing temperature required for PP composite fabrication, the raw/PP, EtOH/PP and NaOH/PP could have had partial burning of hemicelluloses (Johar et al., 2012; Nazir et al., 2013), which also reduce the strength. The higher tensile strength of PEC-US/PP and PEC-AUTO/PP was due to the rod-like crystalline cellulose reinforcing

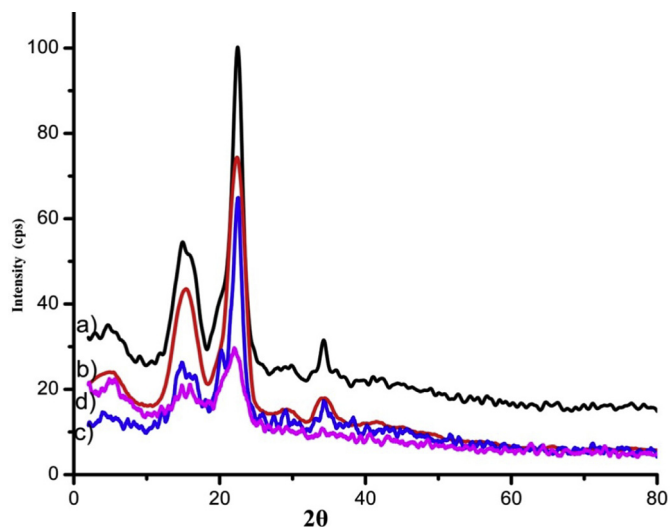


Fig. 4. X-ray diffractogram of (a) commercial microcrystalline cellulose, (b) autoclave-based purely-extracted cellulose (Nazir et al., 2013), (c) ultra-sonicated purely-extracted cellulose, (d) raw empty fruit bunch.

the PP, similar to the filaments dispersed in the matrix. The grooves on the PECs fibers would have taken part in interlocking the fibril with the PP. Well-aligned and oriented fibrils in composite should give better strength and elasticity. The relative stiffness of raw/PP and PEC-US/PP composites were higher, but the raw/PP and PEC-AUTO/PP showed higher elongation (5.6–5.9%) even though the breaking point may be different. These variations suggest that structural defect could occur at random during fabrication as similarly observed with cellulose fillers and kenaf/PP composites (Table 3) (Laka et al., 2011; Ling and Ismail, 2013).

3.4.2. Effects of different PEC loadings

The PECs at 20%, 25%, 30% and 40% loading were blended with PP. Fabrication at 40% PEC was limited by increased viscosity that hindered agitation and uniform mixing with molten PP. The results (Fig. 5b and Table 3) showed that as PEC loading was increased from 10 to 25%, the tensile strength was also increased, but the strength decreased at 30%. Rice straw fibril (RSF)/PP composite also exhibits similar trend (Wu et al., 2009). Without any coupling agent, the tensile strengths (MPa) of PEC-AUTO/PP (27.3) and PEC-US/PP

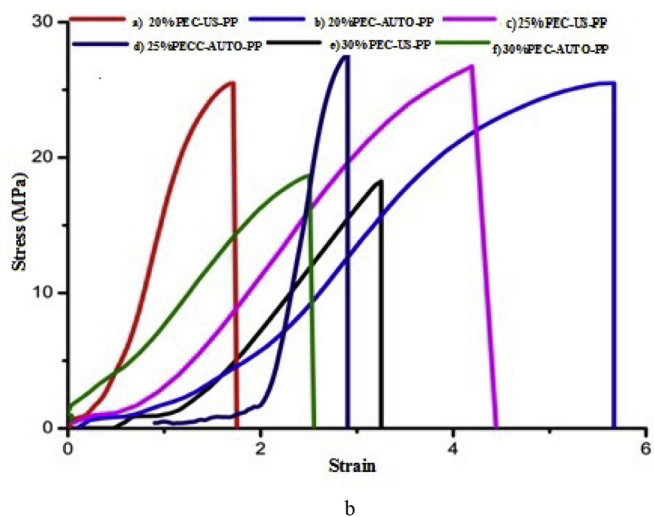
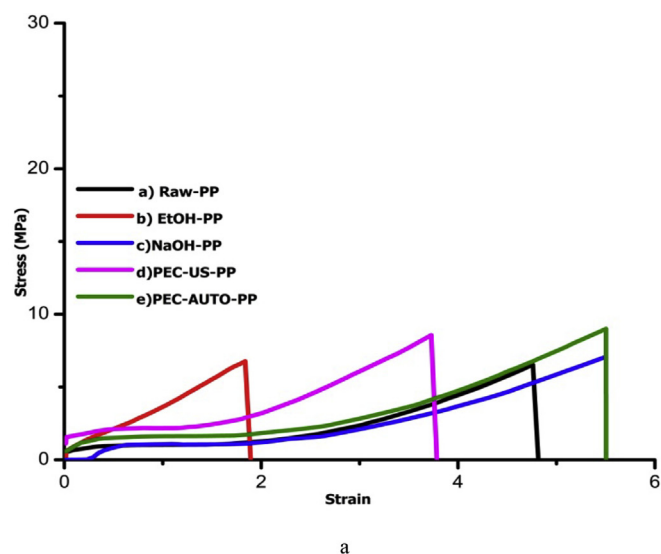


Fig. 5. (a) Tensile strength of (i) Raw/PP, (ii) EtOH/PP, (iii) NaOH/PP, (iv) PEC-US/PP, (v) PEC-AUTO/PP; (b) Tensile strength of (i) 20% PEC-US/PP, (ii) 20% PEC-AUTO/PP, (iii) 25% PEC-US/PP, (iv) 25% PEC-AUTO/PP, (v) 30% PEC-US/PP, (vi) 30% PEC-AUTO/PP (abbreviations as described in Section 2.5).

Table 3
Comparison of mechanical properties of polypropylene and fiber composites.

Composite material	Tensile strength (MPa)	Young Modulus (MPa)	Elongation at break (%)	Reference
Polypropylene	20			Slaughter (2004)
Polypropylene	28.5	1.5 (GPa)		Stark and Rowlands (2003)
Raw/PP (10%)	6.5	389.1	5.64	Our study
EtOH/PP (10%)	7.0	244.5	1.89	
PEC-US/PP (10%)	8.5	306.9	3.76	
PEC-US/PP (10%)	9.0	295.7	5.93	
PEC-US/PP (20%)	20.7	231.3	1.95	
PEC-AUTO/PP (20%)	20.2	288.2	5.82	
PEC-US/PP (25%)	26.8	257.2	4.34	
PEC-AUTO/PP (25%)	27.3	268.4	2.96	
PEC-US/PP (30%)	18.8	179.8	3.15	
PEC-AUTO/PP (30%)	18.4	236.3	2.49	
Saw dust (50%)/PP saw dust (25%), Wood flour (25%)/PP	13.47	1502.2	4.44	Laka et al. (2011)
Waste paper (25%), wood flour (25%)/PP	11.24	890.1	3.32	
Cotton residue (25%), wood flour (25%)/PP	8.9	631.7	3.38	
Pine wood (25%), wood flour (25%)/PP	9.57	717.2	3.36	
Rapeseed oil (25%), wood flour (25%)/PP	12.42	806.1	4.75	
Rapeseed oil (50%), wood flour/PP	20.45	1556.2	3.32	
Rapeseed oil (25%), wood flour (25%)/PP	15.75	1549.0	5.22	
EFB blend in phenol formaldehyde	8.9			
EFB (40%)	9.57	308.1		Zuhri et al. (2009)
EFB (50%)	12.42	372.8		
EFB (60%)	20.45	350.6		
Kenaf/WPT/PP (10%)	15.75	622.1	8.6	Ling and Ismail (2013)
Kenaf/WPT/PP (10%)+ APTES	12.5	665.7	7.4	
Kenaf/WPT/PP (10%)	9.9	718.8	5.6	
Kenaf/WPT/PP + APTES	10.9	759.4	4.5	
Industrial particle board products with code				
A	7.7	2200		McNatt (1973)
B	9.3	2600		
C	8.3	2300		
H	10.9	3000		
J	7.5	1900		
K	5.6	1600		
L	6.7	1800		
M	8.1	2200		
N	8.0	3700		

(26.8) at 25% PECs were higher than the EFB/phenol formaldehyde composites (Zuhri et al., 2009), saw dust and wood flour composites (Laka et al., 2011), kenaf fiber composites (Ling and Ismail, 2013) and industrial particle board (McNatt, 1973). Even with the coupling agent addition, the tensile modulus and strength of the eco-composites from *Eucalyptus globulus* cellulose with residual agricultural plastic films are increased only upto a maximum of 20.26 MPa and 23.96 MPa, respectively (Sanchez et al., 2014). Ultra-lightweight PP composites prepared from cotton stalk cellulose fibers extracted by SFE-AT, with bulk density of 0.27 g/cm³, attain the composites of between 13.7 and 20.3 MPa tensile strength, but the Young's modulus is high between 1660 and 2887 MPa (Hou et al., 2014). Although our developed PECs/PP composite showed high tensile strength, the Young's modulus was low and comparable to EFB/phenol formaldehyde composites, but lower than the saw dust, waste paper, cotton, pine, wood flour/PP, wood particle composites, and kenaf/PP/waste pulverize tire (622–759.4 MPa) (Table 3). The Young's modulus of particle board was almost 10-fold higher suggesting a stiffer material under elastic load. This may suggest the elastic nature of our PECs/PP composites which could be easily molded into shape without rupture. This ductility or ability of a material to deform plastically without fracturing is often characterized by the material's ability to be stretched into a wire under tensile stress. This mechanical property of a material which is also dependent on the temperature and pressure applied has gained wide interest especially in the study of structures or materials for earthquake engineering (Li et al., 1999), which is beyond the scope of our study.

3.4.3. Characterization

3.4.3.1. Morphology. As compared to raw EFB which exhibits tightly-packed compact structure (Fig. 6a), the EtOH/EFB showed rough structure with cavitations due to the partial removal of hemicelluloses and waxy layer (Fig. 6b). The NaOH/EFB also showed partially torn structure which exposed the cellulose strand attributable to these hemicelluloses and partial lignin removal (Fig. 6c). The complete separation of cellulose fibrils in SONO-CHEM-treated and the AUTO-CHEM-treated EFB with punctures and pores on the surface (Fig. 2) from the removal of the elemental particles, is similarly observed in kenaf (Kargarzadeh et al., 2012). After the tensile test, the remaining composites were cut carefully and the morphology investigated. At 10% loading, raw/PP suggests a well-mixed composite (Fig. 6d), also observed in EtOH/PP (Fig. 6e). The NaOH/PP had partial opening and roughness to provide better substrate for the intervening PP, than the raw/PP and EtOH/PP (Fig. 6f).

Both PEC-US/PP and PEC-AUTO/PP showed better filling and intermixing of the PEC with the PP and may have developed joints with the molten PP to give greater reinforcement (Figs. 6g,h and 7a,b). The holes and grooves that appeared may be due to the pulling out of PEC fibers at the break point, leaving behind the scar suggesting the lack of physical and chemical interaction between the fibers and the PP. This explains the lower tensile strength at 10–20% loading. The tight and compact filling of PEC-fibers in the PP matrix can be observed at 25% loading (Fig. 7c and d) resulting in higher tensile strength attributable to the filling of PEC and thin network of PP surrounding the fiber to confer strength. The fibers

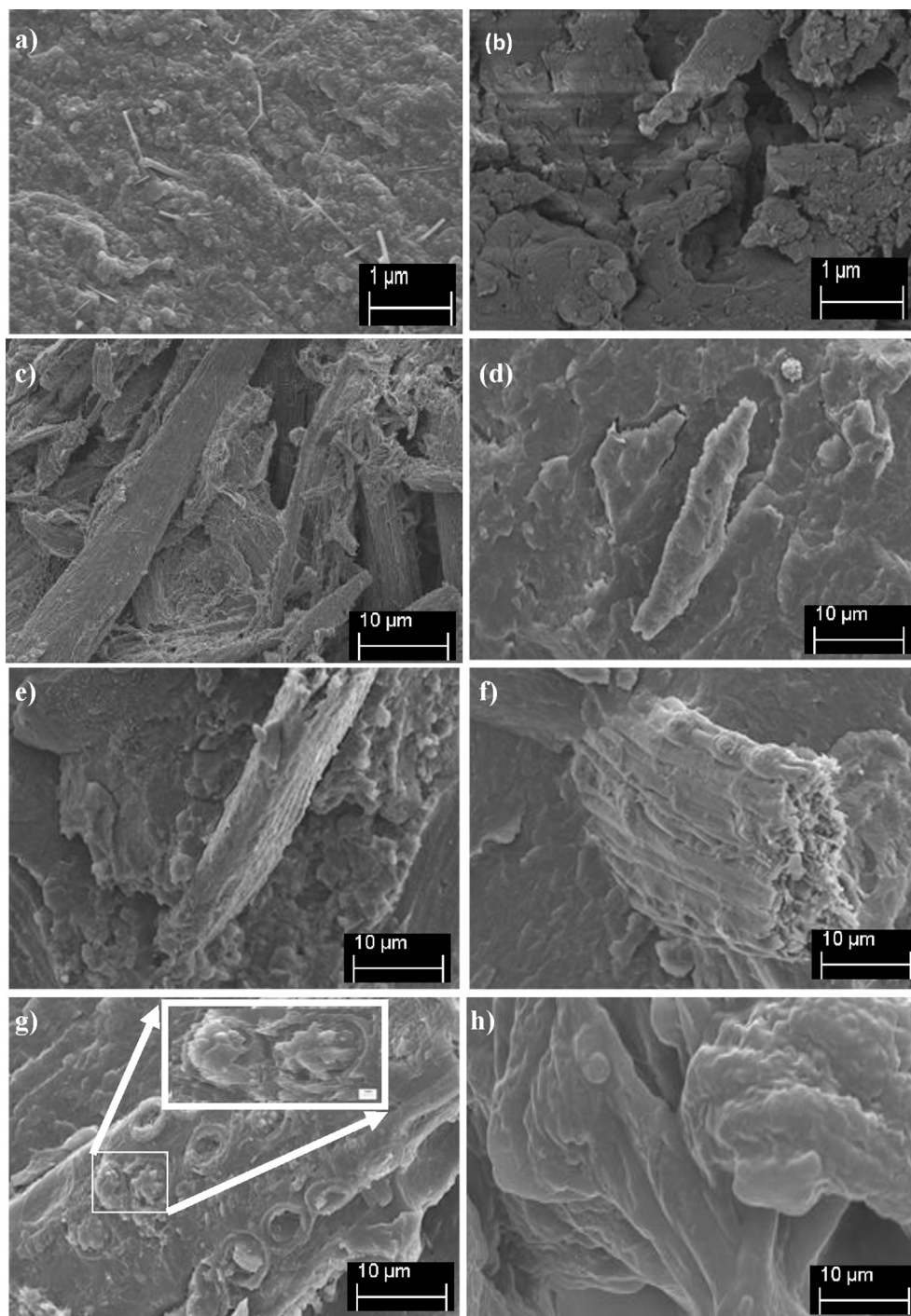


Fig. 6. Field emission scanning electron microscope micrograph of (a) Raw EFB; (b) EtOH-EFB; (c) NaOH-EFB; (d) Raw/PP; (e) EtOH/PP; (f) NaOH/PP; (g) PEC-US/PP; (h) PEC-AUTO/PP at 10% PEC loading (abbreviations as described in Section 2.5).

were completely pulled out, leaving behind thin thread-like structures of PP, suggesting the part of PP intervening the crevices and cracks. The porous PEC structures produced after the removal of metals and silica, allow oriented fiber in the matrix with maximum fusion of PP into the pores and cracks to create high tensile strength. The decline in tensile strength at 30% loading (Fig. 7e and f) can be attributed to less uniform mixing during fabrication as the mixture becomes more viscous, reducing proper fusion of PP into the holes and cracks. Maximum 30% PECs/PP composites even broke under lesser-applied stress.

Similar effects of loading and morphological changes have been reported for the cellulose and wood flour in PP-grafted-maleic anhydride (Ashori and Nourbakhsh, 2010), rice straw fibrils (RSF) in PP (Wu et al., 2009), and raw EFB and 10% NaOH treated and blend with PP (Tay et al., 2010). Saw dust, waste paper, cotton pine and oil-treated wood flour of lignocelluloses have –OH, aldehyde groups (CHO), ketone [R(CO)R], –COOH aliphatic and aromatic groups unexposed or exposed depending on the types of pre-treatment. The PECs polymer has 3-OH groups on anhydroglucose monomer at positions C-2, C-3 and C-6. The polarity is

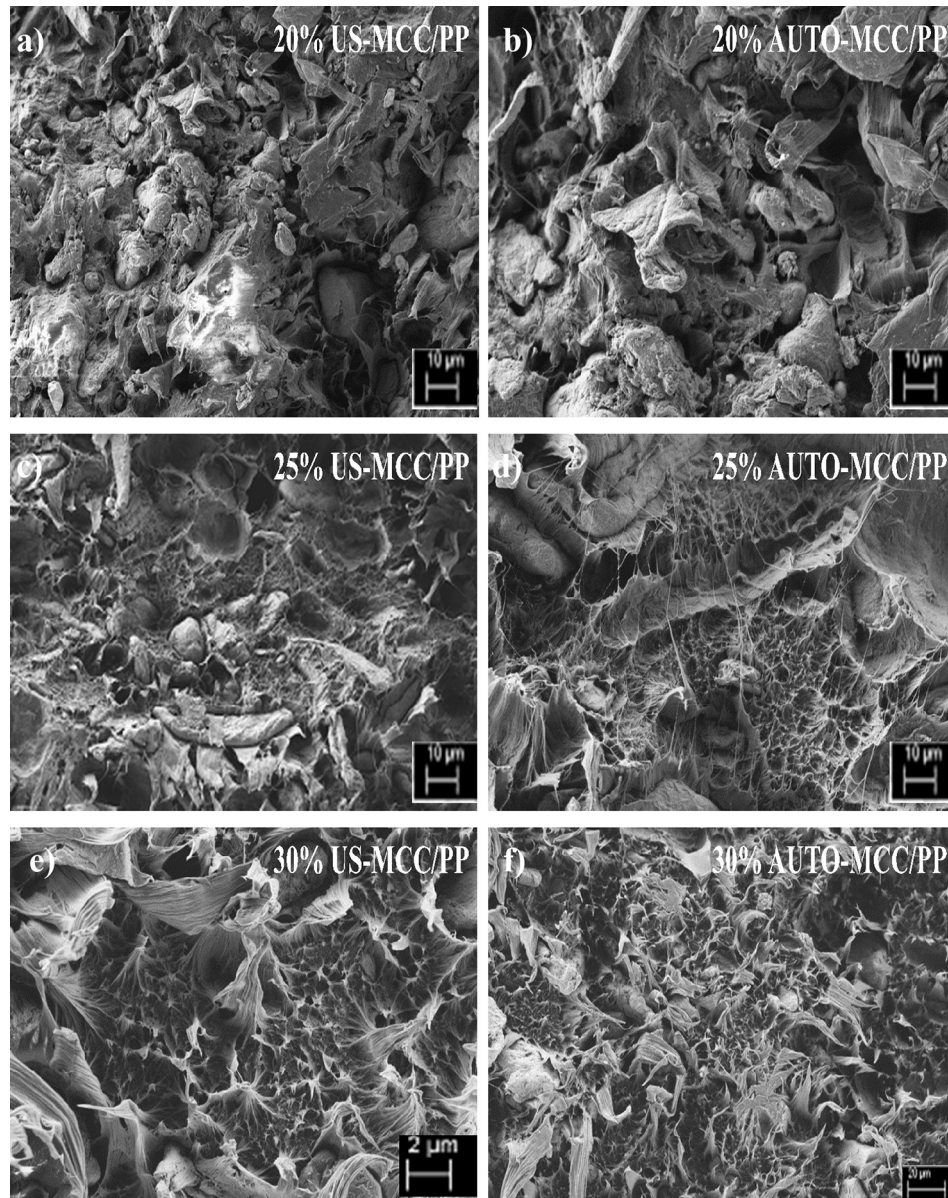


Fig. 7. Field emission scanning electron microscope micrograph of (a) 20% PEC-US/PP (b) 20% PEC-AUTO/PP; (c) 25% PEC-US/PP; (d) 25% PEC-AUTO/PP; (e) 30% PEC-US/PP; (f) 30% PEC-AUTO/PP (abbreviations as described in Section 2.5).

due to the difference in electronegativity of bonded O and H atoms at 3.5 and 2.1, respectively. However, the $-\text{OH}$ of cellulose and $-\text{[CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2\text{]}_n-$ of PP has no interaction (Ling and Ismail, 2013). Addition of the coupling agents can improve interfacial interaction and bonding inter-connection between the hydrophilic fiber and hydrophobic matrix to yield the composite of high mechanical strength. Among these are maleic anhydride (Ashori and Nourbakhsh, 2010), N,N' -*m*-phenylenebismaleicimide (BMI) (Sain and Kokta, 1994), and hexamethylenediisocyanate (HMDIC) (Maldas and Kokta, 1991). Low density polyethylene (LDPE) plastic wastes contain significant amounts of ethylene/vinyl acetate (2.5–4.5 wt%) and the photo-stabilizer which increase its value as matrix for cellulose-reinforced composites. Property variations can be achieved through the addition of the maleic anhydride-modified PE coupling agent which improves interfacial adhesion and causes fiber length reduction and plasticizing effect (Sanchez et al., 2014).

3.4.3.2. Thermogravimetric analysis (TGA). TGA of raw EFB shows weight loss of 10% at 110 °C, representing the loss of resident water molecule (Nazir et al., 2013). The decomposition of raw EFB fiber observed at different points, suggests different compositions of compound that have different stabilities corresponding to the temperature, such as wax, pectin, hemicelluloses which degrade at 180 °C, and cellulose between 300 and 400 °C (Johar et al., 2012). The residual mass after thermal decomposition was more than 20%, possibly due to the accumulation of cellulose, lignin chars (Alemdar and Sain, 2008) and heavy metals. The sharp decomposition at 350 °C was due to the incision and disintegration of cellulose chain into fragments. TGA of PEC showed smooth curve, with only 8% loss of water at 110 °C, and decomposition continued from 350 °C and ended with 8% residual char at 410 °C, comparable to 5% residual mass of commercial MCC at 380 °C. The residual mass of PEC can be attributed to the aromatization of C–C and C–O at much higher temperature such as 400 °C in the absence of oxygen. Thermal

stability of EFB/PEC at 350 °C was higher than soy hulls (290 °C) and wheat straw (296 °C) (Yang et al., 2007) but lower than cotton MCC (380 °C).

TGA of pure PP showed degradation starting from 330 °C (Fig. 8a) which was the degradation of the $-\text{[CH}_2\text{-CH(CH}_3\text{)]}_n\text{-}$ and ended at 400 °C with 2% weight loss. The fibers and cellulose/PP fabricated composites at 10% PEC showed more pronounced thermal stability than singular fiber. Raw/PP and EtOH/PP showed thermal stability at 350 °C, suggesting that the EFB and the EtOH/EFB are not much structurally different when blended with PP. The NaOH/PP however showed the stability at 390 °C and this could largely be due to the complete removal of the hemicelluloses and wax layer although some lignin may still remain. The first degradation peak started in all composites at 350 °C attributable to the PECs decomposition, with pronounced peaks observed at 400 °C with varying weight losses depending on the amount of fibers. Composites with higher relative ratio to PP showed two degradation peaks suggesting uneven distribution of PECs within the matrix. The 20% PEC-US/PP and PEC-AUTO/PP composites (Fig. 8b)

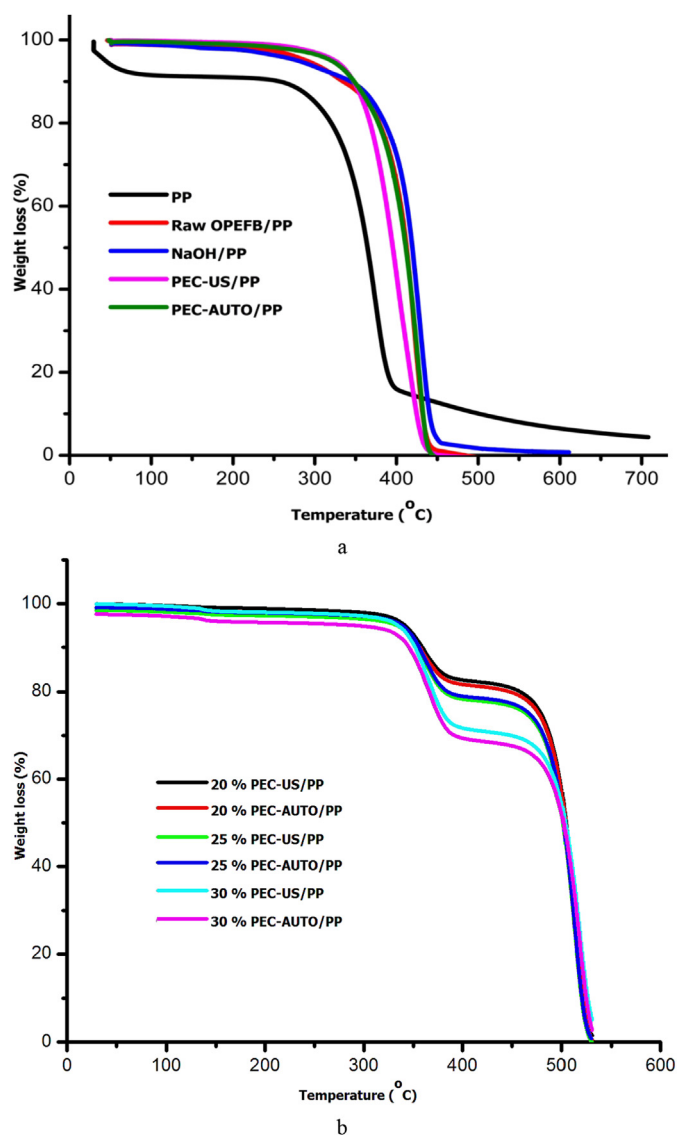


Fig. 8. (a) Thermogravimetric analysis of (i) PP, (ii) Raw EFB/PP, (iii) EtOH/PP, (iv) NaOH/PP, (v) PEC-US/PP, (vi) PEC-AUTO/PP; (b) Thermogravimetric analysis of (i) 20% PEC-US/PP, (ii) 20% PEC-AUTO/PP, (iii) 25% PEC-US/PP, (iv) 25% PEC-AUTO/PP, (v) 30% PEC-US/PP; (vi) 30% PEC-AUTO/PP (abbreviations as described in Section 2.5).

curves showed degradation starting at 350 °C, with 16% weight loss observed at 400 °C. The composites were completely degraded at 575 °C. The 25% PEC-US/PP and PEC-AUTO/PP composites had 22% weight losses at 400 °C with complete degradation at 550 °C. The 30% PEC-US/PP and PEC-AUTO/PP composites had 30% weight loss at 400 °C and completely decomposed at 570 °C. The mixing of cotton stalk fibers with PP reportedly result in a higher T_{max} (383–386 °C) than the standard cellulose (Hou et al., 2014). Our PEC-US/PP and PEC-AUTO/PP exhibited the highest thermal stability at 430 °C which was an enhancement of approximately 150 °C, due to the combined effects of celluloses covering the PP at different ratios which confer increased stability. The fibers and PECs not only reinforced the PP but the PPs may owe their extra thermal stability to the introduction of PECs structure. Thermal and mechanical properties suggest that the PEC/PP composites could be explored as support material for fractured bone, ornamentals articles, house kitchen-wares and mechanical parts of low tension machine (Nazir, 2013; Yu, 2009; Malkapuram et al., 2009).

3.4.3.3. Water and diesel oil sorption. The water absorption in raw/PP and EtOH/PP (data not shown) were 1.11% 1.5% respectively, with full saturation after 15 days, and stayed constant for 30 days. The low uptake may be due to unexposed polar groups and compact lignocelluloses. The water holding capacity of NaOH/PP composite was slightly higher at 2% after 15 days, which can be attributed to the partial exposure of surface. PEC-US/PP and PEC-AUTO/PP showed water holding capacity of 5.5 and 5.4%, respectively, and are attributable to the presence of $-\text{OH}$ groups of PECs available for H-bonding. The water uptake for 20–30% PECs/PP composites achieved full saturation point after 20 days. The 30% PEC-US/PP and PEC-AUTO/PP composites showed water sorption at 8.3 and 8.5%, respectively, higher than the lower PEC loading. The $-\text{OH}$ groups on cellulosic fiber are responsible for holding water molecule by H-bonding, having equivalent polarity with O-H of water which confers the chemisorption of composites (Lejeune and Deprez, 2010). The physisorption of water holding in the composites are due to factors such as cracks, voids, lumens and pores in the matrix. The higher PECs loading in the PP composite, the higher will be the water uptake, but the overall water uptake remained below 10%.

Chemically, diesel should show most favorable interaction with PP and comparatively lesser interaction with cellulose due to its polar $-\text{OH}$ groups. The raw/PP and PECs/PP showed only around 3.7–4.6 g/g oil sorption (data not shown) as compared to 30 g/g reported for kapok fibers with more than 90% dynamic retention (Abdullah et al., 2010). These were far lower than the 10 g/g value reported for the pelletized grain cotton, soft wood with dry cellulose, organic mineral, cellulose minerals, organic with 20% zeolite, organic pecan with minerals and clays (Nazir, 2013). The dynamic retention of diesel in composites was 95–99.9% at which the amount of diesel retained was only 3.7–4.5 g/g. The more compact structure of PEC/PP composites suggests lower hollow lumen or tubular network as compared to kapok fibers for enhanced oil sorption (Abdullah et al., 2010).

3.5. Discussion

Efficient and effective management of resources, emission and biodiversity are key ingredients to sustainable development for healthy economy, environmental quality and social equity. With growing interest towards environmental and sustainability issues, the whole range of input and output processes in the product manufacturing can be made eco-friendly and cleaner. Green solvents, catalysts and media for chemical reactions and processes are

embedded in the Green Chemistry concept with principle objective to achieve reaction efficiency minus the use of toxic reagents, for wastes reduction and effective utilization of resources (Disale et al., 2012). Green cellulose extraction by sonication and autoclave with less hazardous or toxic chemicals, at low temperature and pressure can pave the way for more economical and environmentally-friendly process route. While some pre-treatment techniques may be successful in the laboratory environment especially if the aim is to achieve cellulose of high-crystallinity, the cost-benefit analysis will ultimately determine its suitability especially for large-scale application, the intended final product use and whether or not it meets the industrial standards.

The development of sustainable eco-composites using agro-wastes and natural or cellulosic fibers with recycled materials or plastic wastes are among effective strategies for waste recovery to remediate the environment thus reducing land-filling and improving the sustainability of the products manufactured. These have attracted increasing interest especially within the automobile, construction and food and beverages sectors (Kidalova et al., 2012; Dammer et al., 2013). High-density polyethylene component in the recycled agricultural plastic or post-consumer plastic coming from bottles can be used as matrices for eco-composites with waste cellulose (Urreaga et al., 2015). In construction industry, the increasing demand for environmentally friendly materials and the high cost of synthetic fibers (such as carbon, glass or aramid) have led to the uses of renewable materials, materials recycled from construction waste or new bio-based, low density and lightweight composites. The major challenge is to attain long term durability of natural fiber-reinforced composites due to their elevated permeability and lack of resistance to crack growth. The different properties of each polymer, properly selected, can be combined to create new blends with properties such as the utilization of lime and zeolite as connective alternative admixtures, or active admixtures in composites, which can be even better than those of the neat polymers (Kidalova et al., 2012). For systematic approach, there may be a necessity to categorize the considerable factors and criteria affecting the selection process of the natural fiber composite materials for different applications, to address the potential and capabilities of different fibers and to establish comprehensive criteria as guidelines and database to assist designers in material selection and optimization process (Al-Oqla and Sapuan, 2014). Our study has developed green techniques for cellulose extraction from agro-lignocellulosic wastes using combination of heat and eco-friendly chemicals. The cellulose/polypropylene composites developed with high tensile strength, high thermal stability, and low water and diesel sorption have great potentials for eco-composite product applications such as microfiller in polymeric material insulated cables for high voltage engineering, automotive parts, sports and amusement tools, boats, office and household products and machinery.

4. Conclusion

- Green extraction of PECs from EFB employing ultrasonication and autoclave treatment was successfully developed.
- Cellulose yield at 490 and 640 g kg⁻¹, and the α -cellulose content of 91.3% and 93.7%, respectively, were better than those reported earlier employing non-green chlorite method.
- The SONO-CHEM and the AUTO-CHEM-treated fibers showed complete separation of cellulose fibrils, with punctures and pores on the surface.
- The PECs/PP at 25% fiber loading achieved high tensile strength of 26–27 MPa, without any addition of coupling agents.
- The PECs/PP composites also exhibited the highest thermal stability at 430 °C, with low water and diesel sorption.

- The high thermal and mechanical properties of developed PEC/PP composites may have potentials as support or reinforced materials in insulated cables for high voltage engineering, biomechanical system or recreational, office or household items.

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