

Extraction of Hemicellulose and Lignin from Sugarcane Bagasse for Biopolymer Films: Green Process

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ABSTRACT

A hemicellulose is any of several heteropolymers, such as arabinoxylans, present along with cellulose in almost all plant cell walls. Hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base as well as myriad hemicellulase enzymes. In this study, lignin and hemicellulose was extracted from sugarcane bagasse using the ammonium hydrolysis process. The extraction of hemicellulose was carried out at 25°C (room temperature) with 25% Ammonia Solution. The sugarcane bagasse extract was used together with starch to produce thin films. The films were characterized using Fourier transformed infrared (FTIR), X-ray diffraction (XRD), Thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The FT-IR and XRD analysis of the films confirmed the presence of hemicellulose and lignin. The TGA shows an average of 16.75% and 50.61% for lignin and hemicellulose respectively. The crystallinity index values obtained from XRD showed that film materials were amorphous and have higher values when compared with untreated SCB, due to the partial removal of hemicellulose after ammonium hydrolysis treatment.

1-Introduction

Agricultural waste such as sugarcane bagasse can be obtained in large quantities from sugar and alcohol industries [1]. About 54 million dry tons of bagasse is produced annually throughout the world [2, 3]. Normally, sugarcane bagasse has been used as a fuel to generate power mills [4]. However, a huge quantity of the remaining bagasse is not used and burnt in the fields causing environmental problems. In recent years, many researchers show interest in utilization of agricultural waste to value-added products, such as sugarcane bagasse used as raw materials for industrial applications. For example, Devnarain, et al. [5] researched about production of activated carbon from South African sugarcane bagasse, while Carrier, et al.

[2] researched about the production of char from South African sugarcane bagasse. In addition to that Cardona, et al. [6] and Kumar and Anandjiwala [7] both agreed that bioethanol can be produced from sugarcane bagasse.

Sugarcane bagasse is a rich source of not only cellulose and hemicellulose, represented by L-arabino-(4-O-methyl-D-glucurono)-D-xylan but also in lignin [3]. The two polysaccharides represent about 70% of bagasse. Entwined around the two sugar polymers is lignin, covalently linked to hemicellulose [8]. Sugarcane bagasse contain about 33.5 % hemicelluloses, which can be further utilized to produce other useful applications [1]. The applications of material from hemicelluloses that have been identified include packaging

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films, cationic biopolymers, food coatings, hydrogels and biomedical uses [2, 5, 9].

Hemicelluloses are polymer of xylose, galactose, mannose, arabinose, other sugars and their ionic acids [10]. Moreover, they are usually classified according to the sugar residue present. The hemicelluloses rank next to cellulose as the most abundant natural carbohydrate polymer in biosphere. They are present in all layers of the plant cell wall but are concentrated mainly in primary and secondary layers where they are closely associated with cellulose and lignin [3].

Unlike cellulose, hemicelluloses are not chemically homogenous [11]. Hardwood hemicelluloses contain mostly xylans, whereas softwood hemicelluloses contain mostly galactomannans [3, 11, 12]. Hemicelluloses are relatively tightly bound in the plant cell wall network to lignin and cellulose. It is difficult to separate them without significant modification of their structure [19, 22].

Lignin is a high molecular weight polymer based on phenyl propane units, and is potentially a renewable source of aromatic compounds if an economic means of extracting and depolymerizing it could be developed [3]. Many researched methods were used so far to extract lignin from lignocellulose such as using ionic liquid, high temperature and pressure, mass depolymerisation and the dissolution of cellulose [11, 12, 18, 20]. Traditional methods of extraction lignin from lignocellulose consist of a range of industrial processes for the production of papermaking pulp from wood chip and other fibres [21].

According to Yang et al. [18] lignin structure has many aromatic rings with many branches such that chemical bonds cover an extremely wide range and that leads to wide temperature range (100 – 900) degradation of lignin. Ammonium hydrolysis process considered a simple, low-cost and environmentally friendly method for generating lignin and hemicellulose from sugarcane bagasse was used as a method of extraction. Thus, in this study, the sugarcane bagasse was used to extract hemicellulose and lignin and then make films for characterization processes. A detailed method on characterization of a film has been reported here.

2-Experimental

2-1-Preparation of Sugarcane bagasse extraction

Sugarcane bagasse was attained from Tongaat Hulett Sugar South Africa in KwaZulu Natal. The sugarcane bagasse was first air-dried and then oven dried at 105°C for 24h. The dried sugarcane bagasse was ground prior to use, using a kitchen blender and screened to select the fraction of particles with a size between 0.18 and 0.15 mm. After that, the powder was stored in desiccator until needed. All chemicals were analytical grade, purchased from Laboratory Consumables & Chemicals Supplies CC (South Africa).

2-2-Extraction of hemicelluloses and lignin

The extraction of hemicellulose was done according to the reported method with some modification [12, 13]. The dried powder of bagasse was washed first with ethanol to remove waxy compounds. The dewaxed bagasse contained 42.4% of cellulose, 25.2 % of hemicellulose, 19.6% of lignin and 1.6% of ash on a dry weight basis [11, 12]. Subsequently, the hemicellulose and lignin were extracted from 10g of sugarcane bagasse dried powder with 100 ml of 25% Ammonia Solution. The ration between solid to liquor was 1:10 and the treatment was done at room temperature for 24h. The resulting mixture was filtrated using vacuum extraction process in Fig. 1. This separation process is a method that converts a mixture of chemical substances into two product mixtures. Vacuum extractions apparatus are complete with vacuum pump, gasket, tubing, filter paper, support plate and funnel ring. The fractions were continuously washed by the addition of distilled water. The hemicellulose and lignin filtrate was then stored in a closed beaker.

2-3-Film preparation

Hemicellulose and lignin films were prepared with some modification [11]. Potato starch 2 g was dissolve with the 150ml (A), 100 ml (B) and 50ml (C) of filtrate. 0.8 g Polypropylene glycol 200 was added to each solution. The mixture was stirred with a magnetic stirrer while cooking it at 100 °C for 10 to 20 minutes.

The cooked mixtures were taken off from heat and left in room temperature to cool for 2 – 5 minutes and the solution was casted in food plate and kept in oven to dry at a temperature of 65°C

for 5 – 8 hours. The films were taken out of an oven and placed in a desiccator for 24 hours prior to characterization.

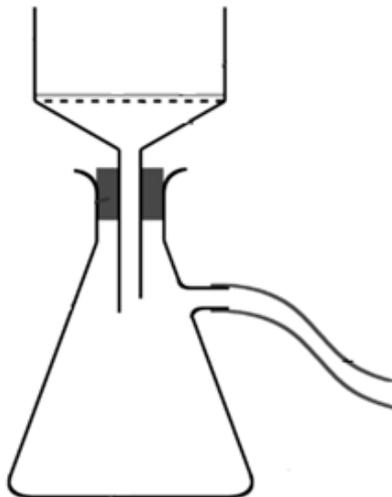


Fig. 1. Vacuum extraction method for extracting hemicellulose and lignin filtrate.

2-4-Characterization of untreated sugarcane bagasse and films

2-4-1-Thickness Measurement

The film thickness was measured by using a thickness gauge (Shirley' thickness). The measurements were taken at 5 different places on the films, and the average value was calculated.

2-4-2-Fourier Transform Infrared (FT-IR) analysis

Chemical properties were tested using Fourier Transform Infrared (FT-IR) Spectroscopy (Varian 800 FT-IR). FT-IR studies on untreated sugarcane bagasse and treated sugarcane bagasse were carried out by dispersing the powdered samples in KBr pellets. All spectra were recorded in the 4000 – 400 cm^{-1} region with a resolution of 4 cm^{-1} .

2-4-3- X-ray Diffraction (XRD) analysis

XRD patterns of a film were recorded on a X-ray diffractometer (PANalytical-Empryan theta-theta) equipped with Co (Anode material) at 40 kV and 40mA Data was collected from 0°C to 90°C Bragg angles (2θ) at a scan rate of 3 deg/min. The crystallinity of lignocellulose biomass accounts for the relative amount of total crystalline cellulose in the solid component. The

crystallinity is strongly influenced by the composition of biomass; the relative amount of lignin, hemicellulose and cellulose varies according to the nature of the biomass. The crystallinity index (CI) was obtained from the ratio between the intensity of the 002 peak (I_{002} , $2\theta = 50.824$) and the minimum dip (I_{am} , $2\theta = 50.214$) between the I_{002} and the I_{am} peaks according to Equation 1 [14]

$$\%C = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

Where I_{002} is the intensity of plane 002 and I_{am} is related to the amorphous structure.

2-4-4-Thermo gravimetric analyses (TGA) analysis

Thermo gravimetric analyses (TGA) of blend film were carried out using SDT Q 600TA Instruments. The specimens were scanned at a heating rate of 10°C/min in the range of 30-600°C in N_2 atmosphere.

2-4-5-Scanning Electron Microscopy (SEM) analysis

The dried films from the desiccator were gold-coated by an electro deposition technique to impart electrical conduction. The morphology of the film was studied using JEOL JEM-7500F (Japan, Tokyo) operating at an accelerating voltage of 2kV.

3-Results and discussion

3-1-Film thickness analysis

Films thickness was measured using 'Shirley' thickness gauge. The film with high volume of sugarcane bagasse had big thickness compared to the rest. The results suggested that film chains could form the compact and ordered film network in the presence of sugarcane bagasse as indicated by the increased thickness. It was plausibly due to the protruded structures mediated by interaction between functional groups of hemicellulose, lignin and potato starch matrix. In general, film thickness depends on the composition of the film forming solution and the nature of its components [3]. Sample A film-forming solution as a consequence of its high water holding capacity swell to large extent, is denser than sample C, which promotes the formation of a thicker film once the solution is dry. The components of the film-forming solution affect the alignment, sorting and compacting of the molecules during film drying process, thereby causing the differences in

thickness. In addition, the interactions between hemicellulose, lignin and potato starch in the composite films resulted in reactions that promoted a change not only in the density of the materials but also in the structure that allowed more water to be retained in film structure resulting in increased thickness. The thickness of a thin film has a critical influence on the stability of the film. It will not discuss more about it here; but one thing should be mentioned here that the glass transition temperature maybe increased or decreased when the thickness of thin film is below a certain limit, depending on the interaction between the polymer and the substrate. For example, Tg of polystyrene(PS) was found to decrease linearly with thickness $h \leq 70$ nm, with a reduction of 70 K for a film with $h=29$ nm [15]. Tg of thin PMMA film on silicon with native oxide layer, how-ever, was found to be slightly higher than the bulk value [19].

Table 1. Thickness measurements of each samples.

Sample	N	Mean	Std. Deviation	Std. Error
A	5	0.4940	0.00894	0.00400
B	5	0.2940	0.00894	0.00400
C	5	0.0980	0.00447	0.00200
Total	15	0.2953	0.16750	0.04325

3-2-Fourier Transform Infrared (FT-IR) Spectroscopy analysis

The FT-IR spectrum of all films are shown in Figure 2. The spectra shows that adding more filtrate bring no conclusion in terms of concentration/bands while the thickness of a film depends entirely on the increase of filtrate which is regarded as the increase of hemicellulose and lignin content. As illustrated in Figure 2, FT-IR spectroscopy shows several major absorption bands representing the typical structure of lignin. The characteristic bands locating in 1455, 1509 and 1602 cm^{-1} indicate the existence of aromatic rings and C-H bonds in the samples [1, 8]. Absorption bands above 1510 cm^{-1} result from carbonyl and aromatic skeletal vibration [1, 15]. Below 1500 cm^{-1} all bands are complex and have their origin in a variety of vibrational modes.

Hemicelluloses are another important group of plant cell wall polysaccharides. Peak intensity at 1734 cm^{-1} is hemicellulose, peaks at 1365 and 1149 cm^{-1} are polysaccharides and peak intensity at 936 cm^{-1} is attributed to cellulose [8, 11]. Furthermore, O-H stretching in methyl groups reflected in the band of 3496 cm^{-1} and this band gives good information about hydrogen bonds formation. Moreover, the bands in the region of 1000 and 1400 cm^{-1} show the existence of C-O or C-H, while the bands in the region of 1230-1210 cm^{-1} indicate the appearance of aromatic phenyl C-O [15, 16]. The behavior of gas product evolving from biomass detected online using FTIR, matched well with degradation of biomass measured using TGA.

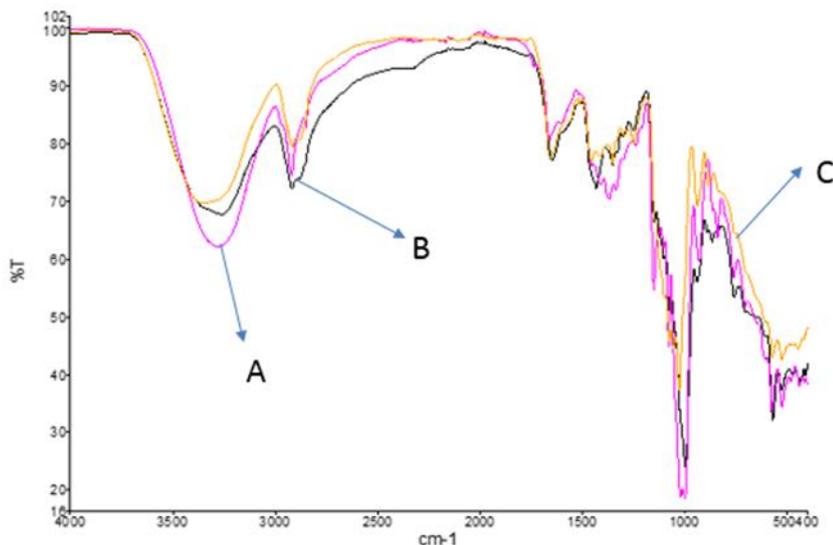


Fig. 2. FTIR spectra of sample, B and C.

3-3-X-ray Diffraction (XRD) analysis

X-ray diffraction patterns shows that polymers were intermediate in order between ideally crystalline solids and liquid-like amorphous materials. Figure 3 shows some similarity between the samples and that is a confirmation that samples (A,B & C) and SCB powered structure are amorphous. As it can be observed, all samples exhibit typical cellulose diffraction peaks, where the highest peak corresponds to the 002 crystallographic planes [4]. The crystallinity index was calculated according to Equation 1

(Methods session). The untreated SCB showed a lower crystallinity (CI = 53.0%) when compared to film (CI = 74.6%) (Figure 3). Many studies indicate that there is an increase in the value of this index when the biomass is subjected to treatment by ammonium hydroxide [17, 20]. The phenomenon is due mainly to the removal of a certain amount of lignin and hemicellulose (amorphous substances) and not necessarily due to changes in the crystalline structure of the biomass.

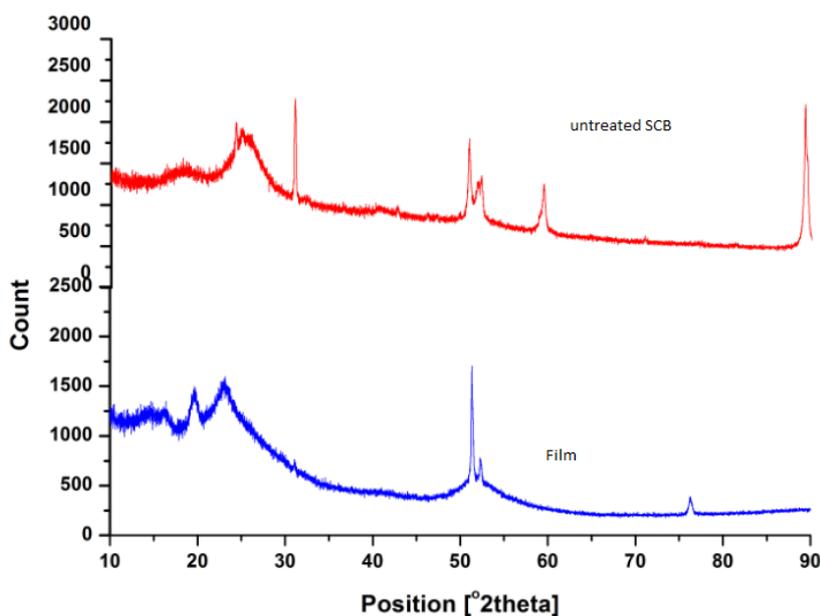


Fig. 3. X-ray diffraction patterns of untreated SCB and film.

3-4-Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) showed significant differences amongst the untreated SCB and films. Figure 5 shows two-steps of decomposition for SCB untreated, which is water and other organic substance present before treatment. The second decomposition is not fully separated this are two organic substance presence. After ammonium treatment figure 6, 7 and 8 had three overlapped clear separated steps leaving less than 20 wt % of residue at 600 °C. TGA analysis for filtrate films shows that the first weight loss of each sample from 25 – 100°C and it was attributed to water and/ or volatile components evaporation corresponding to 8 – 12

wt %. The second and the third steps represent lignin and hemicellulose, respectively. The TGA shows an average of 16.75% and 50.61% for lignin and Hemicellulose respectively. The maximum rates of weight loss were observed between 250°C and 350°C and this was a decomposition of hemicellulose [3, 8, 19,18, 20]. Yang et al [18] further elaborate that pyrolysis of hemicellulose and lignin involves exothermic reactions. This stage is of particular interest in evaluating the thermal stability of the polymer. Filtrate films figures verifies the present of hemicellulose and lignin in all three films samples.

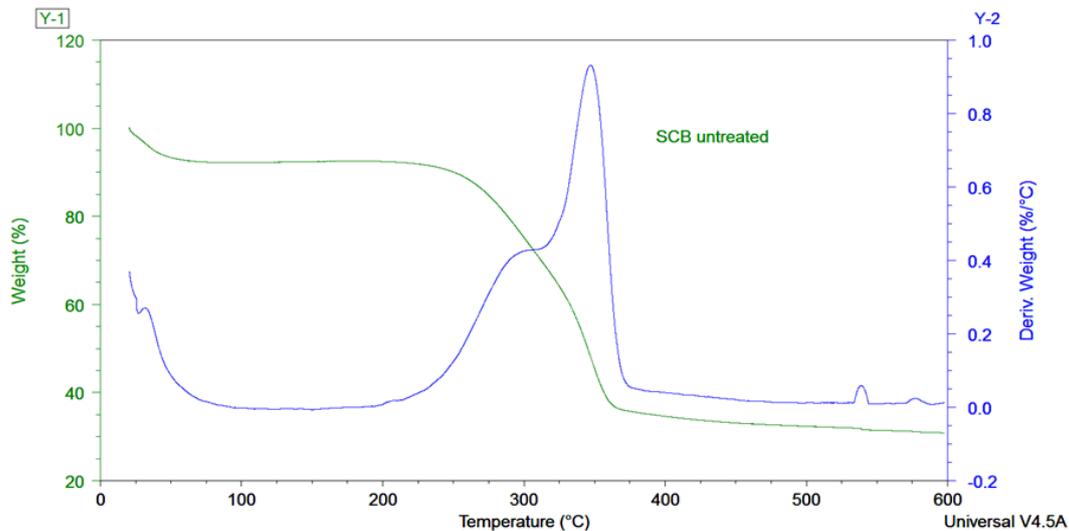


Fig. 5. Thermogravimetric analysis (TGA) analysis SCB untreated.

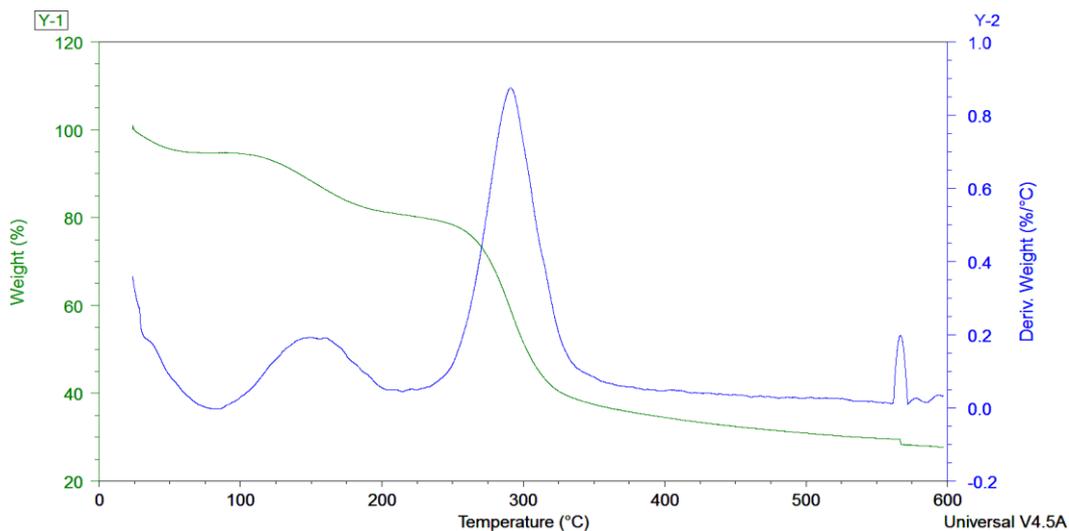


Fig. 6. TGA analyses of sample A filtrate film.

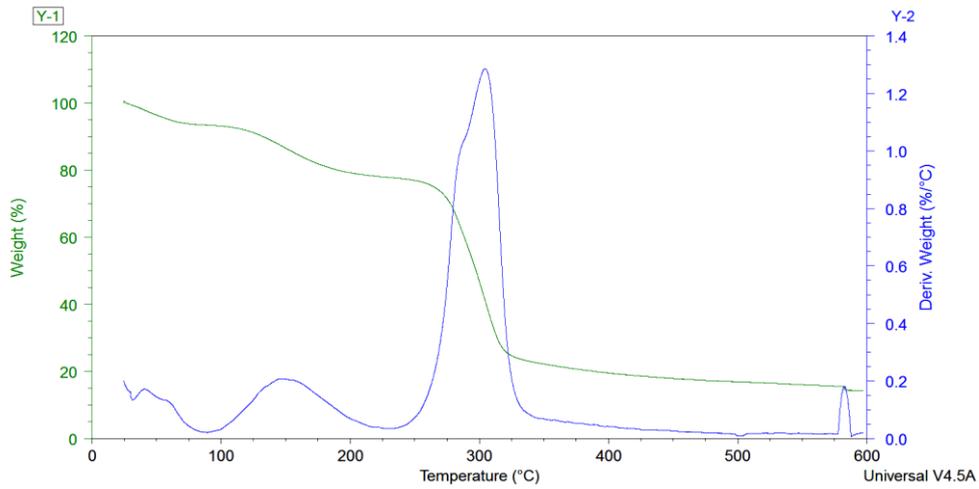


Fig. 7. TGA analyses of sample B filtrate film.

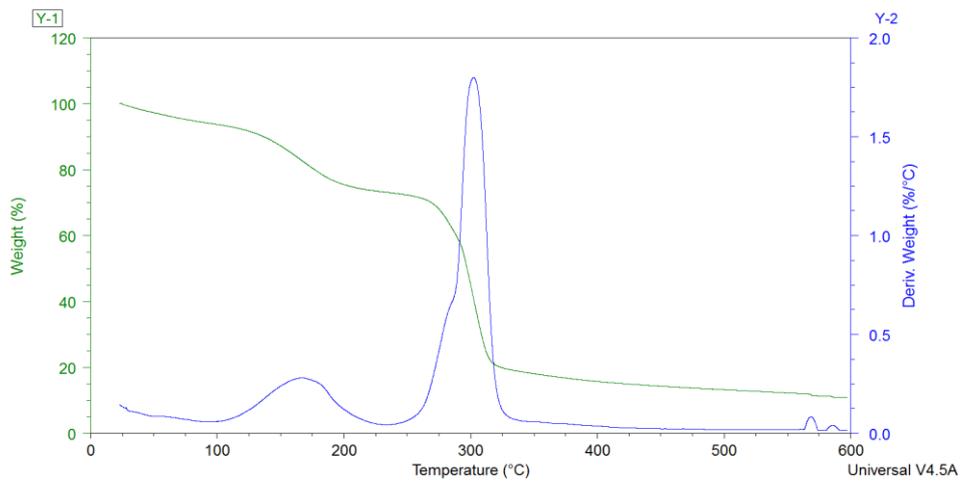


Fig. 8. TGA analyses of sample A filtrate film.

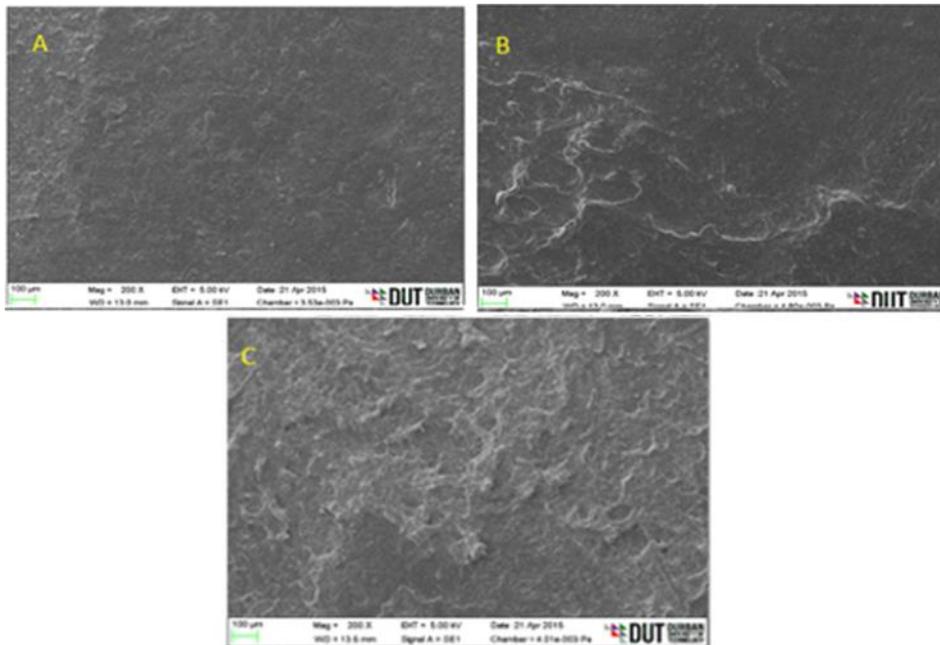


Fig.9. Scanning electron microscope (SEM) micrographs of casted samples film.

3-5-Scanning Electron Microscopy (SEM) analysis

Film materials have the ability of controllable morphology and porosity ratio, adherence to the flexible substrate, and ease of large-area processing. The morphology of films was analyzed using SEM to determine the change of film surface and morphology during the film casting. The surface of sample A presented the smooth and without any cracks or pores surface which revealed a better film homogenisation of the extract. Comparatively, the surface of other films (B and C) showed the rougher surface, which was due to the alignment, sorting and compacting of the molecules during film drying process. In the polymer film, the level of ordered packing determines the efficiency of photon absorption and the diffusion length of exciton. When the crystallinity of polymeric comparatively strong, the diffusion length of excitons and the absorption efficiency of photons increase, facilitating the improvement of short-circuit current [19, 21, 23].

Conclusions

The present study shows that hemicellulose and lignin has been extracted successfully by alkaline hydrolysis technique. The FTIR reveal the present of lignin and hemicellulose in the films and that is confirm through functional groups that are presents in FTIR analyses figures. Lignin showed higher CH₄, while hemicellulose showed CO and CO₂ at higher yield. XRD results revealed that the untreated sugar cane bagasse had a lower crystallinity value (CI = 53.0%) when compared to film (CI = 74.6%). Thermal stability, TGA also indicated the highest yield of hemicellulose compare to lignin was in sample A film. The TGA shows an average of 16.75% and 50.61% for lignin and Hemicellulose respectively. The results suggest that the disposed of bagasse could be developed as a source of hemicellulose and lignin which can be in inexpensive and useful in green composite applications. Overall, the use of ammonium hydrolysis process to extract lignin and hemicellulose has been successfully demonstrated.

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