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THERMAL PROPERTIES OF OIL PALM FIBRE, CELLULOSE AND ITS DERIVATIVES

ROSNAH MAT SOOM*; WAN HASAMUDIN WAN HASSAN*; AB GAPOR MD TOP* and KAMARUDIN HASSAN*

ABSTRACT

Oil palm empty fruit bunches (EFB) are abundantly produced in palm oil mills from processing the fresh fruit bunches. Holocellulose, a composite of hemicelluloses and cellulose, was extracted from EFB using acidified sodium chlorite method. The α-cellulose was then separated from the holocellulose using 17.5% sodium hydroxide solution. Sodium carboxymethylcellulose (Na CMC) was synthesized from the α-cellulose by etherification with chloroacetic acid. The thermal properties of the EFB fibre, holocellulose, cellulose and Na CMC were studied with a thermogravimetric analyser (TGA) in the temperature range 50°C-850°C with nitrogen as purge gas until 700°C and then oxygen for combustion. The cellulose was more resistant to heat than the holocellulose and EFB fibre. The maximum rate of decomposition, or carbonization, for the cellulose occurred at 377.3°C whereas the temperatures for the holocellulose and EFB fibre were 344.4°C and 332.4°C, respectively. The thermogram profiles of the three materials differed from that of Na CMC in the later stage of the heating up to 700°C. The maximum rate of degradation for Na CMC occurred at 329.9°C. On introduction of oxygen at 700°C, combustion occurred and the approximate carbon contents of the materials may be inferred from their final loss in weight.

Keywords: empty fruit bunches, holocellulose, cellulose, sodium carboxymethylcellulose, cellulose derivatives.

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INTRODUCTION

Oil palm empty fruit bunches (EFB) are readily available in large quantities in palm oil mills. It was estimated that the amount of EFB available in Malaysia in a year is about 4.43 million tonnes (dry wt) (Joseph and Chandran, 2002). At present, 65% is incinerated and the bunch ash recycled back to the plantation as fertilizer. However, incineration for bunch ash is not environmentally acceptable due to the emission of white smoke with some fly ash. Empty fruit bunches are also valuable biomass residues which can readily be converted into energy. It has an energy content of 3700 Kcal kg^{-1} (dry weight). In some mills, the empty bunches are pressed to reduce the moisture content and then burnt as fuel to generate steam. Making products of higher value from the empty bunches is another strategy for increasing revenue (Yusof *et al.*, 2001). In this strategy, the EFB can be made into panel products (medium density fibreboard, particleboard), fine chemicals, pulp and paper and can also be blended with synthetic polymers to produce composite materials.

The EFB fibre contains important constituents, such as lignin 18%-23% (w/w), α-cellulose 35% (w/w) and hemicellulose 25% (w/w) (Abdul Azis *et al.*, 1989; Yojiro *et al.*, 1990; Mohamad *et al.*, 1999; Rosnah *et al.*, 2000). The α-cellulose, the major component, is a linear polymer of individual anhydrogluco (glucopyranose) units, joined together by β–1,4-glycoside bonds. The α-cellulose, also termed dissolving pulp or chemical cellulose, refers to a chemically refined bleached pulp of high cellulose content (95% to 98%) with very little lignin (less than 0.05%). It is insoluble in the 17.5% sodium hydroxide solution used to isolate the EFB fibre. It can be chemically converted to other valuable derivatives such as cellulose acetate (Rosnah *et al.*, 2000; 2001; Wan Hasamuddin *et al.*, 2000), cellulose

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* Malaysian Palm Oil Board,
P. O. Box 10620,
50720 Kuala Lumpur,
Malaysia.
E-mail: msrosnah@mpob.gov.my

nitrate (Isniah *et al.*, 2001) and cellulose ethers (Xiao *et al.*, 2001; Rosnah *et al.*, 2002).

Commercially important cellulose derivatives are those of the ether groups. Amongst the ether groups, the most important material is carboxymethylcellulose (CMC), generally prepared by adding chloroacetic acid to sodium cellulose. CMC serves as binding agent and also thickener for a variety of products. Various studies on the thermal behaviour and other properties of cellulose and chemically modified cellulose have been made. Cheng-Y-Lii *et al.* (2002) studied in detail the properties of CMC-gelatin complexes including their thermal and spectra profiles. Natsuki *et al*. (1999) ascertained that the difference in thermogram profiles of deoxyhalocellulose and deoxy-fluorocellulose is due to the difference in their bonding energies.

This paper reports on the preparation of Na CMC from oil palm EFB and the thermal properties of EFB fibre, holocellulose, α-cellulose and Na CMC.

MATERIALS AND METHODS

Preparation of Fibre, Holocellulose, Cellulose and Na CMC

EFB fibre passing through a mesh of 0.25 mm was used for the cellulose preparation. The dried fibre was first delignified according to ASTM, D 1104-56. About 4.0 g of the fibre was then mixed with distilled water and the sample treated with 2.0 ml acetic acid and 5.0 g sodium chlorite at 70ºC for 4 hr. The homogenate was filtered and the residue, which was the holocellulose, was washed with distilled water. This process was to remove the lignin, leaving the hemi- and holocellulose as residue.

The next step was to remove the hemicellulose according to ASTM, D 1103-60. About 2.0 g of the residue was treated with 50 ml 17.5% sodium hydroxide solution, then 70 ml distilled water added. The insoluble α-cellulose was filtered off and washed with 50 ml 8.3% sodium hydroxide. The cleaned α-cellulose was used as the starting material for preparation of Na CMC.

The conversion of α-cellulose to Na CMC was in two stages. Firstly, about 4.0 g α-cellulose in 200 ml isopropyl alcohol were treated with 30% (w/v) sodium hydroxide solution for 1.5 hr to produce alkali cellulose. The second stage involved alkylation, or etherification, of the alkali cellulose with monochloroacetic acid at 55ºC with stirring for 4 hr to give Na CMC. The Na CMC, together with the EFB fibre, holocellulose and α-cellulose were then analysed for their thermal properties.

Thermal Analysis

Thermogravimetric analyses (TGA) of the samples were carried out using a Perkin Elmer Pyris series – TGA 6. The EFB fibre, holocellulose, α-cellulose and Na CMC were analysed over a continuous increase in temperature from 50°C to 850°C at a heating rate of 10°C min^{-1}. The analyser was purged with nitrogen (20 ml min^{-1}) from 50°C to 700°C and then with oxygen (20 ml min^{-1}).

RESULTS AND DISCUSSION

Themogravimetric analysis is a method used to measure the thermal stability of materials. The weight change with temperature was measured and used to infer the moments of change during the heating. The rate of change (a derivative) is often preferred since it clearly marks the point of maximum change in the degradation of the material. The temperature at which the rate of maximum degradation occurs may be taken as an indicator of the stability of the material in comparative studies.

The TGA curves for the EFB fibre, holocellulose and α-cellulose used are shown in *Figures 1, 2* and *3*, respectively. There are similarities in the TGA profiles. In these figures, the weight loss of moisture, volatile compounds and carbohydrate polymers during the oxygen-free pyrolysis (carbonization) phase are shown. Since the derivative curves directly reflect the change in weight with temperature and are often more dramatic, they can be used for comparing similar materials. Generally, there are three peaks in each derivative curve. The first pertains to the release of moisture and volatiles, occurring as the temperature is increased to 200°C. The second indicates structural change in the material normally observed at above 200°C. The third peak indicates the oxidation when oxygen is introduced into the TGA system.

The EFB fibre, holocellulose and α-cellulose contain approximately 7.5%, 6.9% and 8.8% moisture, respectively (*Table 1*). In the second peak, the maximum rate of degradation of the fibre occurred at of 332.4°C, lower than those for holocellulose (344.4°C) and α-cellulose (377.3°C). This indicates that the cellulose was more resistant to heat than the holocellulose and EFB fibre. The reason for the maximum rates of decomposition for the EFB fibre and holocellulose occurring at lower temperatures may be due to the presence of hemicellulose in them. Cellulose is more thermally stable than hemicellulose and more heat energy is needed to break down its crystalline structure and to cleave its macromolecules because of the hydrogen bonds that provide much of the binding energy for α-cellulose. Dietrich *et al.* (1984) reported that the energy of the hydrogen linkage is 460 kJ.mol^{-1}, while the energy of other linkages, such as –C-O, -C-H, and -C-C, are slightly lower at 356, 414 and 347 kJ.mol^{-1}, respectively.

The weight change in the second peak varied with the material as shown in *Table 1*. The degradation of the fibre was 66.2%, holocellulose 73.8% and cellulose 77.4% from 200ºC to 700ºC. On introduction of oxygen at 700°C, combustion occurred and the final weight loss infers the amount of carbon in each sample. The carbon contents of the fibre, holocellulose and α-cellulose were 20.2%, 18.1% and 9.6% (w/w), respectively. The high carbon content of the fibre was due to its other organic polymer constituents, such as lignin. On combustion, all the three materials produced low amounts of ash (*Table 1*).

Figure 4 shows that the thermogram of Na CMC differs from that of α-cellulose. There are also three peaks in the derivative curve. The Na CMC contains approximately 13.8% moisture as indicated by the first peak. This shows that Na CMC is hygroscopic. In the second peak, the maximum rate of carbonization of Na CMC occurred at 329.9°C, very much lower than for cellulose (377.3ºC) and slightly lower than for holocellulose and EFB fibre. The reasons for this are unclear but the ether groups (OCH_2CH_2COONa) on the anhydroglucose units of the Na CMC polymer may have conferred a less crystalline behavior. The maximum weight loss was approximately 37.4%. There is a noticeable shoulder on the second peak which suggests a secondary change at this high temperature side of the thermogram. A possible cause could be decarboxulation. Overall, the weight loss from 200ºC to 700ºC was approximately 47.6%. The calculated carbon content of Na CMC was about 17.9%, as shown by the third peak of the derivative curve. The ash content was approximately 20.6%, higher than for the EFB fibre, holocellulose and cellulose. The ash is usually the salt of an organic acid, normally the sodium salt.

The chemical reactions and physical changes brought about by the conversion of cellulose to Na CMC may have affected both the molecular structure and bonding energy of the material, and caused the different thermal behaviour of Na CMC. Cellulose has a highly ordered structure with each glucose unit its molecular chain bearing three free hydroxyl groups. Intermolecular hydrogen bonds with high bonding energy create a solid-state polyalcohol, making it stable to heat as shown in the thermogram. One of the chemical reactions in the production of Na CMC from cellulose involves a precursor (alkali cellulose) prepared from cellulose in an alkali medium. Migration of Na^+ into the cellulose lattice planes disrupts the hydrogen-bonded crystalline region, causing the cellulose to undergo complete de-crystallization. The energy bonding of cellulose is thus weakened. At this stage, the OH-groups of the cellulose molecule are replaced by ONa-groups, enlarging the molecule. This swelling probably increases the reactivity of –ONa towards alkylating agents and may account for the formation of carboxylmethylcellulose. Since the crystalline region of cellulose has been disrupted, the energy bonding of its derivative Na CMC is also affected and thus Na CMC becomes less stable to heat than cellulose as shown in the thermogram.

In this experiment, the preparation of Na CMC from EFB fibre was by a conventional method which involved chemicals such as sodium hydroxide and chlorine dioxide. These pose environmental hazards and research should be done on processing EFB into Na CMC with less or no chemicals.

TABLE 1. TGA PERCENTAGE WEIGHT LOSS WITH TEMPERATURE FOR EMPTY FRUIT BUNCH (EFB) FIBRE, HOLOCELLULOSE, CELLULOSE AND Na CMC

Sample		(Nitrogen) 1st peak	(Nitrogen) 2nd peak	(Oxygen) 3rd peak	Ash (%)
EFB-fibre	Temperature (°C)	<200	332.4	736.8	
	Weight loss (%)	7.5	66.2	20.2	5.3
Holocellulose	Temperature (°C)	<200	344.4	728.3	
	Weight loss (%)	6.9	73.8	18.1	0.6
Cellulose	Temperature (ºC)	<200	377.3	727.5	
	Weight loss (%)	8.8	77.4	9.6	3.4
Na CMC	Temperature (°C)	<200	329.9	724.3	
	Weight loss (%)	13.8	37.4	17.9	20.6

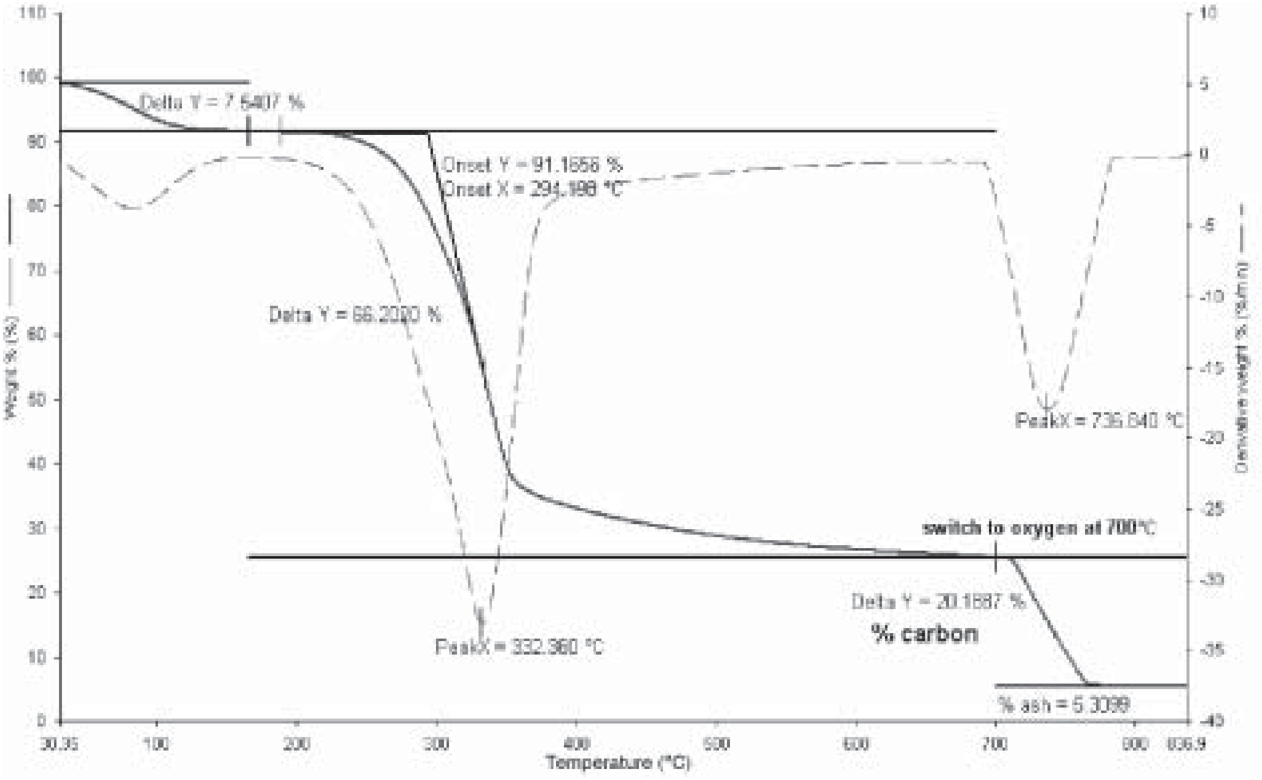

Figure 1. Thermogravimetric profile of an empty fruit bunch (EFB) fibre.

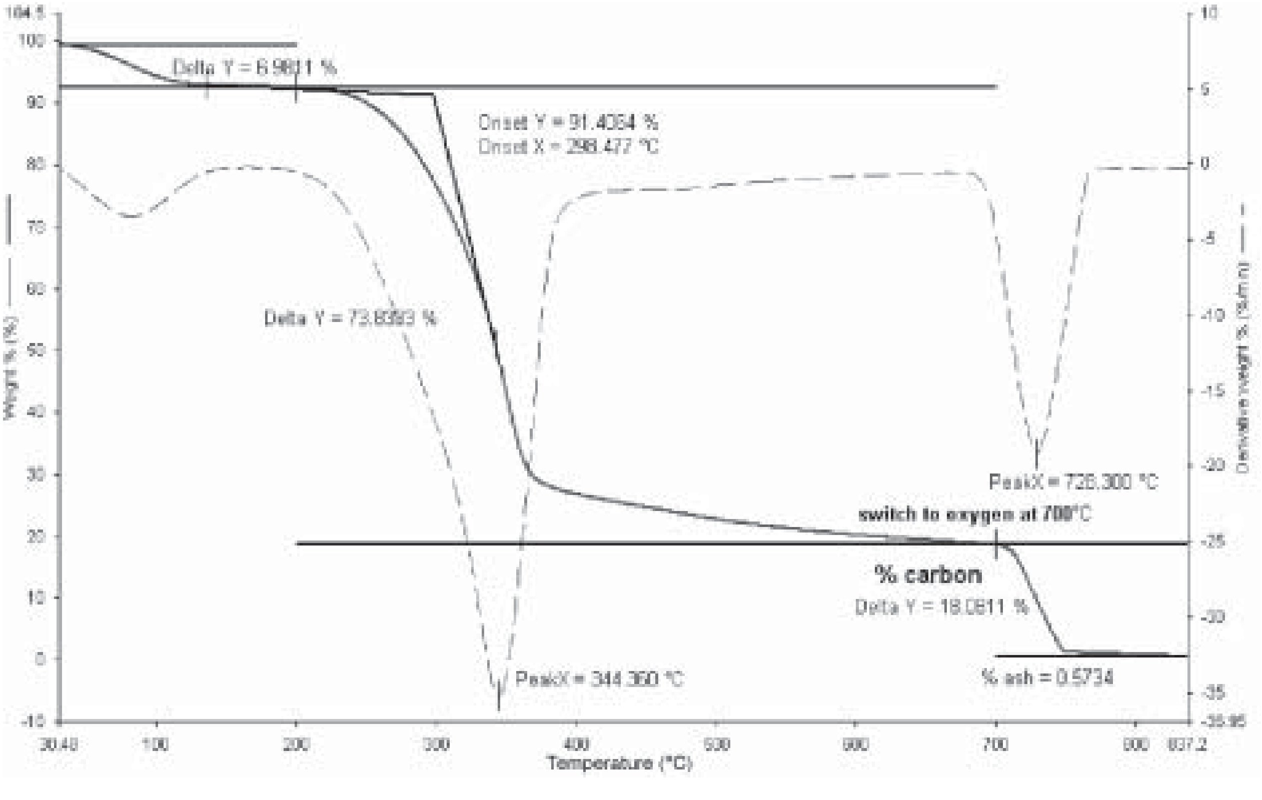

Figure 2. Thermogravimetric profile of holocellulose from empty fruit bunch (EFB) fibre.

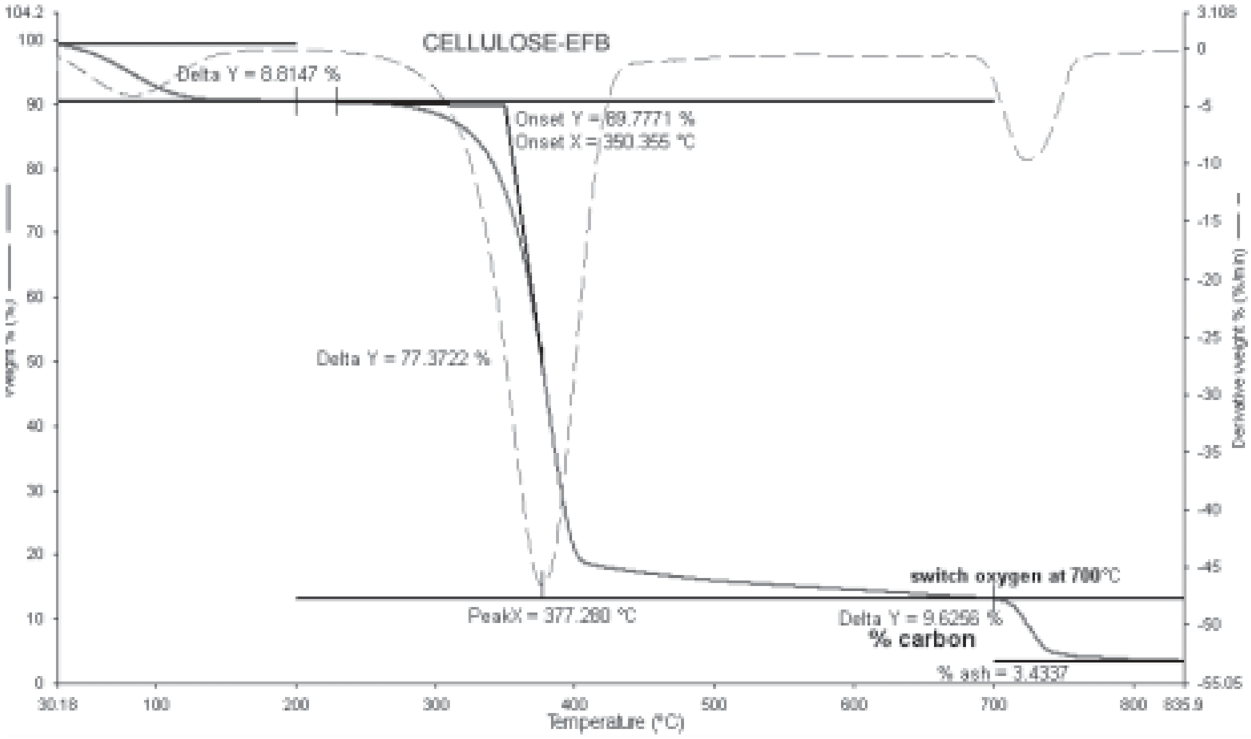

Figure 3. Thermogravimetric profile of α-cellulose from empty fruit bunch (EFB) fibre.

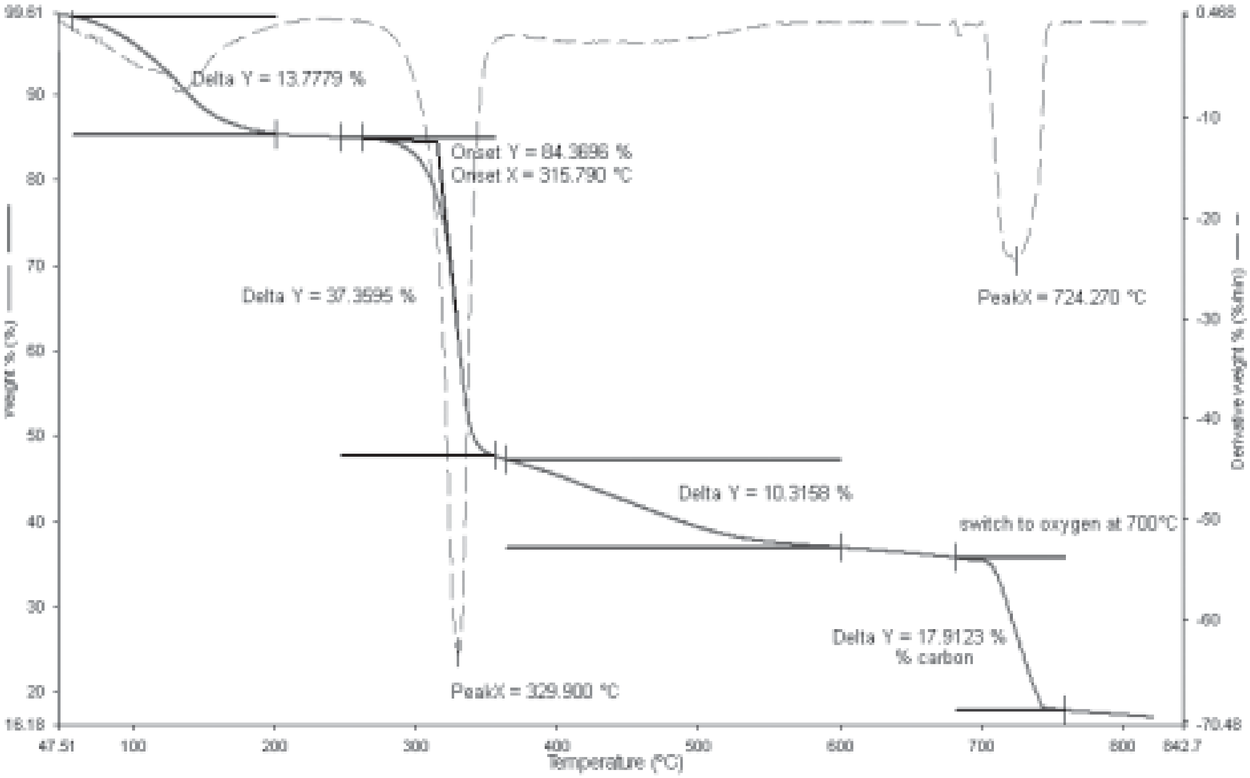

Figure 4. Thermogravimetric profile of sodium carboxymethylcellulose of empty fruit bunch (EFB) fibre.

CONCLUSION

EFB fibre, holocellulose and α-cellulose produced similar TGA curves, but not Na CMC. The α-cellulose was the most heat stable compound of the four materials tested. This was due to its crystalline structure which allowed its maximum rate of degradation to occur at a higher temperature (377.3ºC) than for holocellulose (344.4ºC), EFB fibre (332.4ºC) and Na CMC (329.9ºC). The difference between the TGA curves of Na CMC and α-cellulose was shown to be an additional thermal effect demonstrated on the high temperature side (>330ºC) of the Na CMC curve. The Na CMC was also less stable to heat compared to α-cellulose. The chemical reactions that occurred changed the energy bonding and thermosetting properties of α-cellulose in its conversion to Na CMC.

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