
Thermal characteristics of batch-processed biodegradable cellulosic fibres

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Abstract: Thermal characteristics of processed macro-fibres from five agricultural wastes have been studied. Cellulosic fibres for composite applications are extracted from groundnut shell, coconut shell, rice husk, palm bunch and palm stalk using two paths (M1 and M2) and characterised for improvement in thermal behaviour. Thermal degradation and stability of the processed fibres are characterised using thermo gravimetric analysis and differential scanning calorimetry (DSC). Results show that M2-treated fibres generally possess higher heats of dehydration than M1-treated fibres and this is an indication of superior thermal behaviour of M2-treated fibres. Differential thermal gravimetry curves show that M2-processed fibres contain higher percentage of cellulose content than M1, which shows the removal of lignin and hemicellulose during degradation. Decomposition activation energy of fibres confirms that M1 fibres require higher activation energy for decomposition than M2. Higher degradation temperature is noted for M1-treated fibres than M2-treated fibres.

Keywords: cellulosic fibre; thermal stability; thermal degradation; heat of dehydration; activation energy.

Reference to this paper should be made as follows: Akpan, E.I., Adeosun, S.O., Lawal, G.I., Balogun, S.A. and Chen, X.D. (2015) 'Thermal characteristics of batch-processed biodegradable cellulosic fibres', *Int. J. Microstructure and Materials Properties*, Vol. 10, Nos. 3/4, pp.172–184.

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1 Introduction

Over the last decade there has been renewed interest in the use of natural plant fibres to replace glass fibre in composite applications. A review of cellulosic fibres from plants sources shows that quality fibres suitable as reinforcement in composites can be extracted from maize stems and hulls, rye straw, rice straw and husk, banana bundles, switch grass, wheat straw, sorghum stems and leaves, pineapple, coconut, nettle, velvet, empty palm fruit bunch, hemp, flax, kenaf, cotton, soy hulls and straw, milk weed stems, hop stems and bamboo (Adeosun et al., 2012).

Considerable research has been published regarding the mechanical properties of individual plant fibres; quality fibres have been extracted from hemp by chemical modification for textile and technical applications (Kostic et al., 2008). Hemp fibres are modified with sodium hydroxide solutions (5% and 18% w/v), at room and boiling temperature both under tension to extract non-cellulosic substances and separate the cellulose fibre bundles. The process generally resulted in fine hemp fibres, with low lignin content, increased flexibility, and in some cases tensile properties are improved.

The possibility of using sorghum leaves and stems to produce natural cellulose fibre with properties suitable for composite, textile and other high value fibrous applications is examined by Reddy and Yang (2007). The fibre is extracted using simple alkali treatment and characterised for mechanical, structure and physical responses using standard methods. The breaking tenacity and elongation of the fibres are reported to be similar to that of natural cellulose fibres such as kenaf and cornstalk fibres. However, the sorghum

fibres is found to have a modulus of about 113 g/denier (15 GPa) similar to the modulus of cornstalk fibres but higher than that of cotton and cornhusk fibres. Reddy and Yang (2009) show that natural technical fibres can be extracted from soybean straw with properties similar to the natural cellulose fibres in current use. A simple alkaline extraction is used to obtain the fibres and the composition, structure and properties are then studied. The fibre is found to have breaking tenacity (2.7 g/den, 351 MPa) and breaking elongation (3.9 %) higher than those of fibres obtained from wheat straw and sorghum stalks.

However, natural fibres present some disadvantages such as high moisture sorption, poor dimensional stability, low thermal resistance, anisotropic fibre resistance and variability (Bessadok et al., 2007). Research has shown that these plant fibres contain cellulosic fibrils embedded in lignin with hemicellulose, pectin and wax. The cellulose fibrils which are the major structural component of plant cell walls exist as long fibres with smaller structural units called micro-fibrils, which, in turn, consist of aggregates of elementary fibrils. The size of the micro-fibrils varies with the degree of aggregation of these elementary fibrils and depends largely on the cellulose source (Bertran and Dale, 1986).

The work of Bertran and Dale (1986) confirms that there are two distinctly different regions within cellulose micro-fibril: one of highly ordered cellulose molecules called the crystalline area and the other of less highly ordered cellulose molecules called the amorphous area. Though there may not be a sharp boundary separating the area of high molecular order from that of disordered amorphous fractions, there is, however, a gradual transition from the highly crystalline regions to the completely amorphous areas.

The high quantity of non-cellulosic components in natural fibres (hemicelluloses, lignin, pectin and waxes) and impurities negatively influences further fibre processing and fibre properties (Kostic et al., 2008). The predominant task in preparing natural fibres for further processing is to remove these non-cellulosic components in order to improve fibre properties without damage to the fibre (Kostic et al., 2008). Individual methods used for processing natural fibres include steam explosion, alkaline treatment, thermal alkaline degradation, shear alkaline peroxidation, silane treatment, acid hydrolysis and high pressure homogenisation (Adeosun et al., 2012). These methods prove to achieve improved mechanical and chemical properties of fibres. However, the adhesion property does not significantly improve. The adhesion properties of fibres depend basically on the amount of non-cellulosic materials present in the fibre structure. A well-designed process that can reduce the presence of non-cellulosic materials without damage to the fibre is necessary.

The capacity of cellulose fibres for water absorption depends largely on the availability of free hydroxyl groups. It is assumed that water absorption occurs almost entirely in the amorphous regions of cellulose, neglecting the free hydroxyl groups that may be present on the surfaces of the crystallites. Crystalline areas of cellulose absorb very small amount of water, and water sorption in cellulose occurs almost entirely in the amorphous regions; hence, cellulose moisture content (accessibility to water) is directly proportional to the amorphous fraction of cellulose. Thus, the amount of heat required to dehydrate a cellulose sample can be taken as a direct measure of its amorphous fraction (Bertran and Dale, 1986). The area of the endothermic peak (a measure of the heat of dehydration) due to loss of absorbed water during thermal degradation is directly related to the amorphous fraction of cellulose (Ciolacu et al., 2011). Therefore, measurement of

the heat of dehydration can be used as a measure of the amount of amorphous substance in the fibre as well as the effectiveness of the treatment given to the cellulosic fibres.

Most treatments given to natural fibres focus on removal of hemicellulose and lignin to enhance crystallinity and surface properties. Since the thermal decomposition of wood products depends mostly on its main components, namely hemicellulose, cellulose and lignin (Gašparović et al., 2009), a study of thermal degradation of treated fibres should be able to account for the functionality of the treatment that is given. Thus thermal degradation and stability analysis of fibres serve as measure of the functionality of the treatment method.

This study is designed to investigate the effect of two designed treatment paths on the surface quality of fibres through thermal, degradation and stability characterisations of the fibres. Thermo gravimetric analysis (TGA) is used to study the thermal degradation behaviour and thermal stability using activation energy. Attempt is made to correlate the measured thermal properties and amount of non-cellulosic content of the fibres. To study the effectiveness of two treatment paths designed for this study on the removal of amorphous portions of the fibres, differential scanning calorimetry (DSC) tests are conducted.

2 Experimental methodology

2.1 Materials

Palm stalk, palm bunch, rice husk, groundnut shell and coconut shell are the agro wastes used for this study. These waste materials are collected from farm fields in Ekpoma, a city located in southern Nigeria. The unwanted parts are removed and the fibrous sheaths dried in air for two weeks. Each agro-waste material is subjected to two processing paths designated M1 and M2. These treatments are done at the National Institute of Science Laboratory Technologist, Ibadan, Nigeria.

The study plant wastes are collected, washed, dried in sunlight, cut into small pieces, ground to pass a screen of 10 mm in a mechanical crusher and divided into two. The first set (M1) is subjected to steam explosion at 175°C and 1bar in an autoclave. Alkaline hydrolysis is conducted on the resulting fibre in 2% solution of NaOH overnight, neutralised in acetic acid and bleached with 8% solution of hydrogen peroxide. Further acid hydrolysis is undertaken with a mixture of 10% (w/w) nitric acid and 10% (w/w) chromic acid at a temperature of 60°C for 15 min. The second set (M2) of fibres is first de-waxed with benzene–ethanol treatment in a Soxhlet extractor, washed to neutrality and oven dried at 45°C. The resulting fibres are subjected to steam explosion at 175°C and 1bar in an autoclave. Enzymatic hydrolysis is carried out on the resulting fibre using 50 mL of 50 mM sodium acetate buffer (pH 4.8) at 50°C for 2 h. This is followed by alkaline hydrolysis, bleaching and acid hydrolysis as done in the first set. All treated fibres are then washed in water, centrifuged in ethanol and dried in still air.

2.2 Differential scanning calorimetry

To study the thermal characteristics of fibres, the study fibres are dried in an oven at 100°C for 6 h, and about 5 mg fibre sample is weighed in an aluminium pan, covered with an aluminium lid and closed using a press. The DSC Q200 machine uses nitrogen gas to cool the flange of the heater. The DSC curves of celluloses are obtained with

minimum and maximum temperatures of 40°C and 200°C, respectively, at a heating rate of 10°C/min. The samples are heated to 200°C, cooled to 40°C and heated again to 200°C. The heats of dehydration are estimated using a data analysis software to integrate the peak areas between specified temperatures and to calculate the corresponding energy changes. For each DSC curve, the peak maximum temperature is first determined, and the integration then performed between the temperature $T1 = T_{\text{peak}} - 60^\circ\text{C}$ and $T2 = T_{\text{peak}} + 60^\circ\text{C}$.

2.3 Thermo gravimetric analysis

To study the thermal degradation behaviour of the processed fibres, the thermal-induced weight loss of the sample is measured through dynamic and isothermal heating by a thermo-gravimetric analyser (SII TG/DTA 6300, EXSTAR 6000). Samples are dried in an oven at 100°C for 6 h before the start of the experiment. The thermo-gravimetric experiments are conducted on disc samples of approximately 1 mg under pure nitrogen gas flow. The derivative thermogravimetry (DTG) is also obtained. A single heating run with heating rate of 10°C min⁻¹ from 30°C to 750°C is used.

3 Results

3.1 Effect of treatment of thermal behaviour of fibres

Figures 1–5 show DSC curves for all the processed cellulose fibres, with endothermic peaks appearing between about 100°C and 140°C for all samples. The DSC curves for groundnut shell fibres shown in Figure 1 are characteristic curves of the native cellulose of cellulose 1 structure. The peak of M2-treated fibres appears below that of M1-treated fibres. The difference in peak temperature observed here shows the effect of treatment on the thermal behaviour of the fibres. Groundnut shell – M1 possesses higher peak temperature (133.14°C) to groundnut shell – M2 (121.77°C). Figure 2 is a plot of the DSC scans for coconut shell fibres with typical native cellulose structure. The curve for M2-treated fibres appears above that of M1-treated fibres contrary to that of groundnut shell fibres. However, similar to groundnut shell fibres, the peak temperature is highest for M1-treated fibres (125.69°C). Similar to coconut husk fibres, the DSC scan for rice husk fibres (see Figure 3) shows a typical native cellulose structure with the curve of M2-treated fibres lying above that of M1-treated fibres. The peak temperature is also found to be higher for M1-treated fibres than for M2-treated fibres. Figure 4 shows the DSC scan of palm bunch fibres. The curves seem to be similar but with a large difference of the peak temperature. The temperature of dehydration of palm bunch fibre M1 (109.17°C) is higher than that of palm bunch fibre M2 but with a lower peak area corresponding to a lower heat of dehydration. The DSC scans of palm stalk fibres shown in Figure 5 are typical native cellulose curves with similar features. The scan indicates the presence of water of dehydration during the first scan leading to a peak temperature at 118.32°C and 122.28°C for palm stalk M1 and palm stalk M2, respectively. Palm stalk M2 shows a higher peak area, indicating a higher heat of dehydration.

Figure 1 DSC plot of processed groundnut shell fibres (see online version for colours)

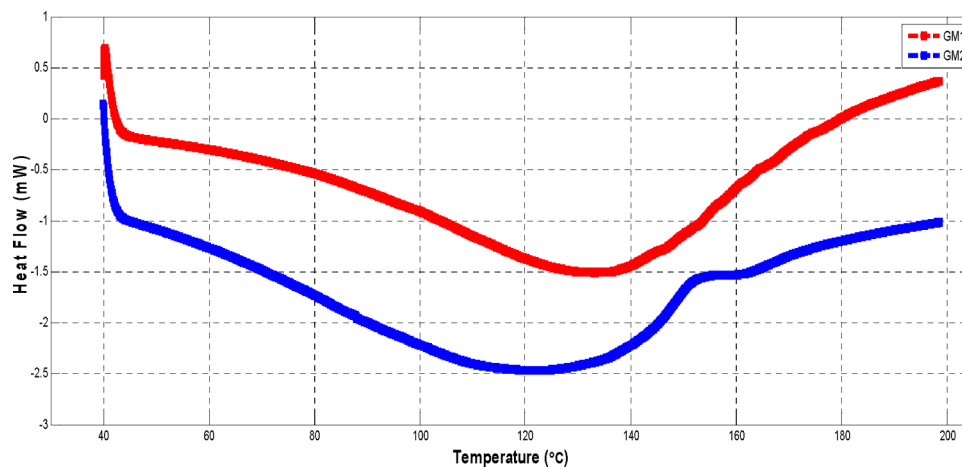


Figure 2 DSC plot of processed coconut husk fibres (see online version for colours)

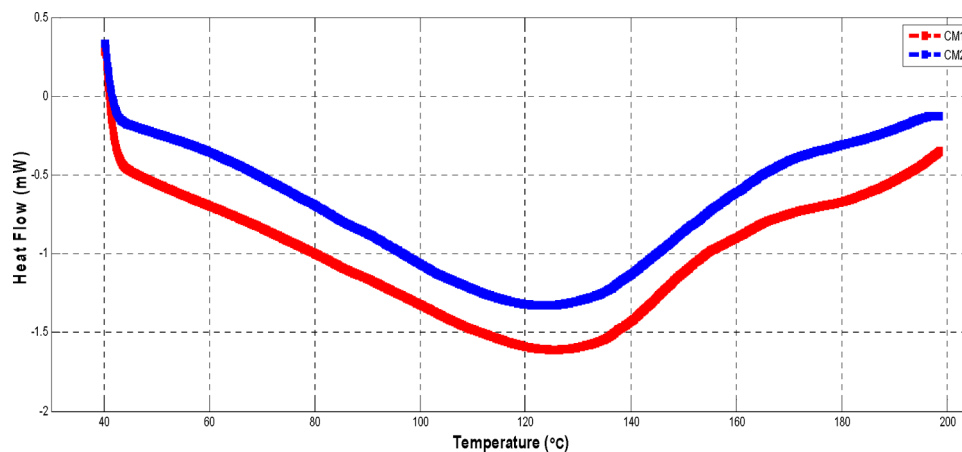


Figure 3 DSC plot of processed rice husk fibres (see online version for colours)

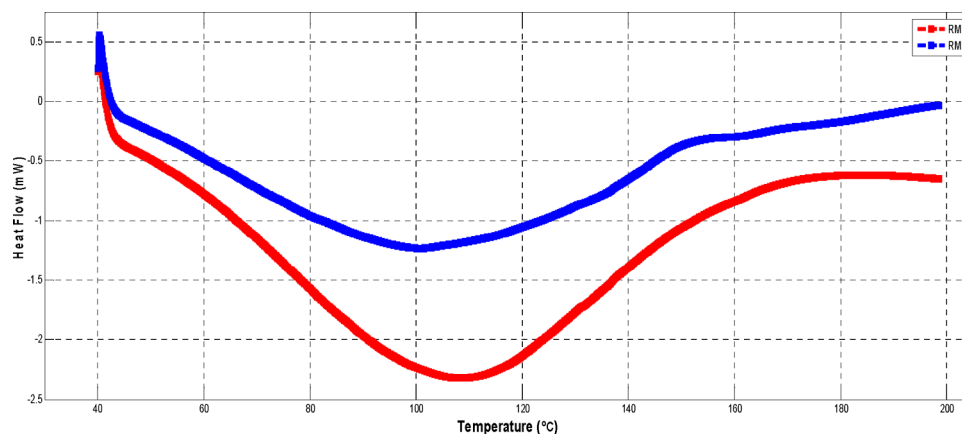
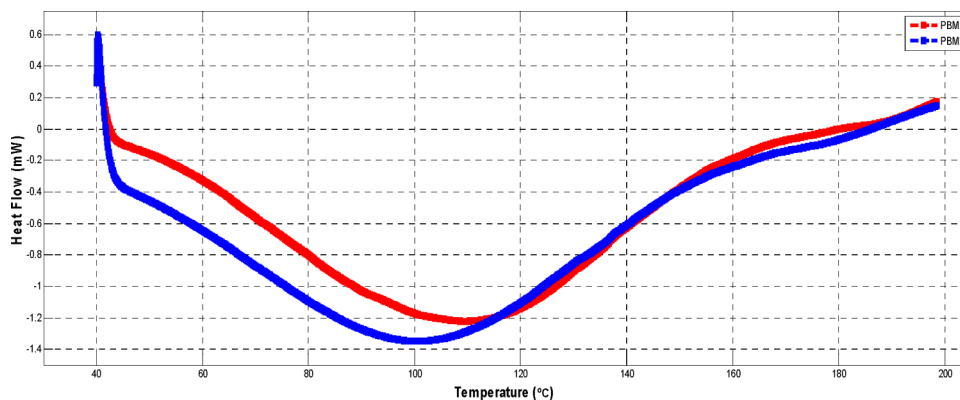
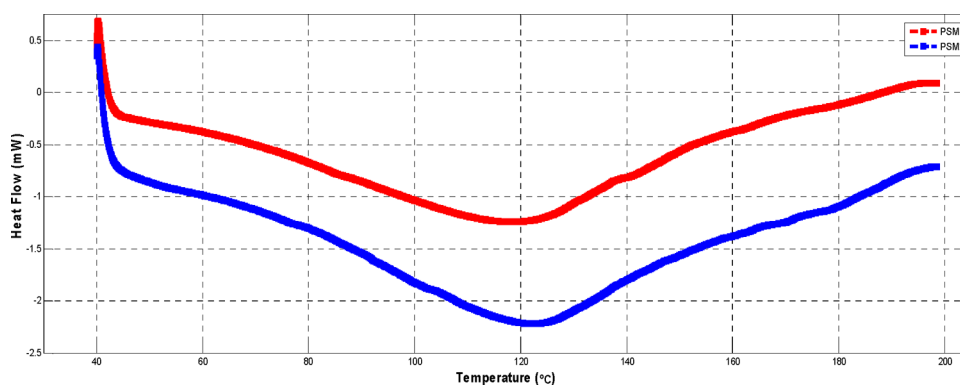


Figure 4 DSC plot of processed palm bunch fibres (see online version for colours)**Figure 5** DSC plot of processed palm stalk fibres (see online version for colours)

3.2 Effect of treatment on thermal degradation of fibres

Figure 6 presents the differential thermo gravimetric decomposition process of natural fibres at a heating rate of 10°C/min. The DTG curves present the rate of fractional conversion and the TGA curves show the percentage weight remaining over the temperature range. The peaks between room temperature and 120°C are attributed to the removal of residual water in the fibres. Rice husk fibres M1 shows an obvious ‘shoulder’ which is normally considered as the result of thermal decomposition of hemicelluloses in an inert atmosphere (Yao et al., 2008). Cellulose decomposition peaks are shown at 349.5°C by groundnut shell M1 followed by coconut shell M2 at 335.9°C and 355.6°C for rice husk fibres M1. Groundnut shell M1 peak is the highest peak followed by coconut shell M2 and rice husk M1. Figure 7 shows the TGA curves for the fibres. Groundnut M1 fibres show gradual degradation of the fibres from the starting temperature of 32.14°C to the onset of degradation at 269°C, but increase rapidly afterwards till 349.5°C. Similarly, rice husk M2 fibres show gradual degradation from a starting temperature of 31.95°C to the onset of degradation at 290°C, but increase rapidly afterwards till 335.9°C. For coconut shell M2 fibres, a gradual degradation is noticed between starting temperature of 19.54°C to the onset of degradation at 284°C, but increases rapidly afterwards till 355.6°C.

Figure 6 Differential thermal gravimetry of processed fibres (see online version for colours)

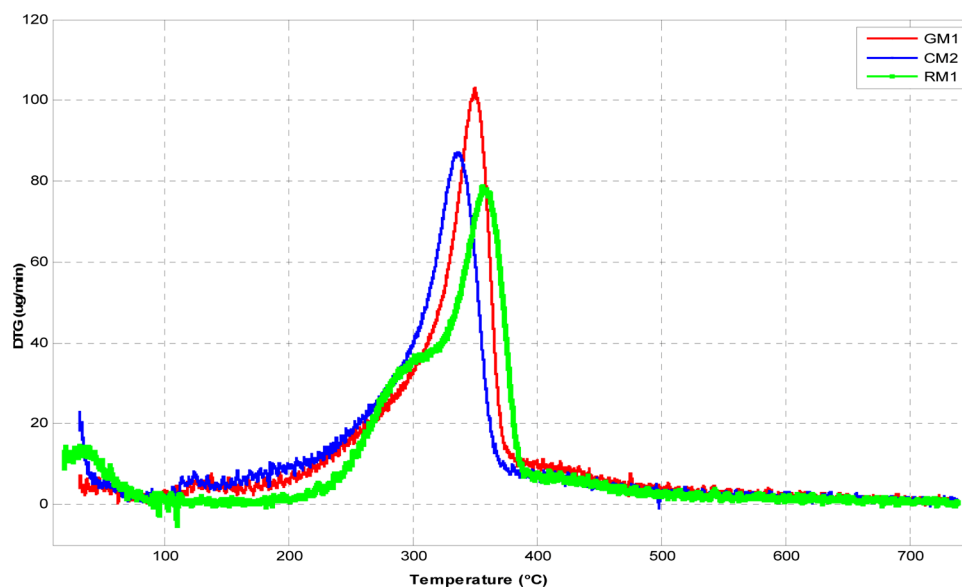
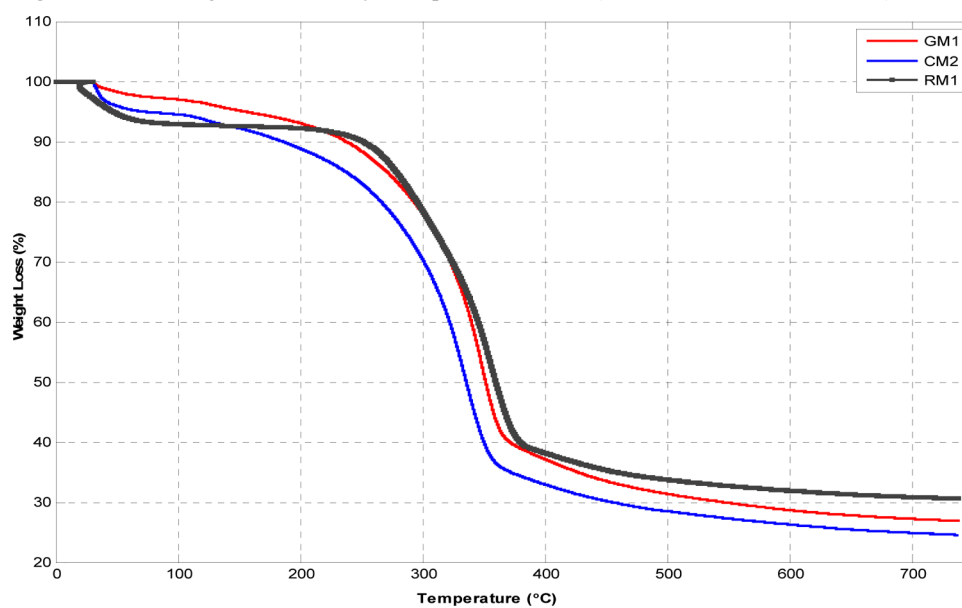


Figure 7 Thermo gravimetric analysis of processed fibres (see online version for colours)



4 Discussion

4.1 Thermal behaviour of processed fibres

The DSC curves of all fibres (see Figures 1–5) are characteristic curves of the native cellulose of cellulose 1 structure with endothermic peaks appearing between 100°C and

140°C and are in agreement with the studies of Betran and Dale (1986) and Ciolacu et al. (2011). The peaks are assumed to be caused by dehydrated water, which disappear on cooling and during rescanning through the same temperature. The peak temperatures are regarded as dehydration temperatures for the fibres. The area of this peak is directly proportional to the endothermic heat flow caused by the physical change(s) in the sample water desorption from cellulose and evaporation (dehydration). The energy changes produced during cellulose dehydration is calculated by measuring the peak area of each endotherm (see Table 1). Fibres processed via M2 show lower dehydration temperatures and higher peak area than fibres processed via M1. Table 1 shows that groundnut fibre M2 sample has a higher heat of dehydration than groundnut fibre M1. Since the amount of heat required to dehydrate a cellulose sample is a direct measure of the amorphous fraction (Betran and Dale, 1986), it is evident that M2 fibres contain more amorphous portion than M1 fibres.

Table 1 Heat of dehydration of the processed fibres

<i>S. No.</i>	<i>Sample</i>	<i>Dehydration temperature (°C)</i>	<i>Heat of dehydration (J/g)</i>
1	Groundnut shell -M1	133.14	16.65
2	Groundnut shell -M2	121.77	31.62
3	Coconut shell-M1	125.69	25.14
4	Coconut shell-M2	123.41	20.27
5	Rice husk-M1	108.45	39.58
6	Rice husk-M2	100.78	21.09
7	Palm bunch-M1	109.17	16.33
8	Palm bunch-M2	100.82	22.07
9	Palm stalk-M1	118.32	15.79
10	Palm stalk-M2	122.28	33.71

Coconut shell fibre M1 is seen to have a higher temperature of dehydration but lower peak area than coconut shell fibre M2. This implies that coconut shell fibre M1 has a higher heat of dehydration (see Table 1). Thus the treatments used do not produce the same effect on fibres as observed earlier with groundnut shell fibre M1 having a higher heat of dehydration than groundnut shell fibre M2, but a reverse occurrence in the case of processed coconut shell fibres. This may be attributed to the differences in composition, initial percentage amorphous content and the physical nature of the cellulosic materials used in the study. Considering the rice fibres, both treatment paths produced samples having endothermic peaks. This is attributed to the removal of water of dehydration from the cellulose samples during the cyclic heating and cooling. The curve of the second heating shows a straight line, which is an indication that the water of dehydration is completely removed at the first scan. It can be deduced (see Figure 3) that rice husk fibre M1 possesses a higher temperature of dehydration and a higher peak to rice husk fibre M2 with resultant higher heat of dehydration and consequently a larger volume of amorphous content. A comparison of the scans in the region of the endothermic peaks show that M1 has the highest effect on palm stalk fibres followed by palm bunch in terms of removal of amorphous fraction, while M2 is effective on rice husk fibres followed by

palm bunch. These results show that the appropriate method for treating any cellulosic material is dependent on source, composition and physical nature of the cellulosic material examined. From this study M1 is better used for palm bunch and stalk while M2 is suitable for rice husk, coconut shell and maybe palm bunch fibre.

4.2 Overall decomposition process of fibres

Thermal degradation curves (see Figure 6) show that rice husk M1 has a 'shoulder' which is considered the result of thermal decomposition of hemicelluloses in an inert atmosphere (Yao et al., 2008). These low-temperature hemicelluloses' shoulder peaks, however, overlapped in the cellulose main peaks for coconut shell M2 and groundnut shell M1 although not obvious. This is attributed to rice husk M1 fibres containing more hemicellulose portion than both coconut shell M2 and groundnut shell M1 fibres. It is inferred that coconut shell M2 and groundnut shell M1 contain less amorphous portion than rice husk M1, and consequently should have higher crystallinity than groundnut shell M1. This is evident from the DSC result where the heat of dehydration of rice husk M1 is higher than that of groundnut shell M1 and coconut shell M2 (Table 1). The high-temperature 'tails' shown for all fibres are displayed by the degradation of lignin (Yao et al., 2008; Antal and Varhegyi, 1995). The 'tails' are only prominent between 400°C and 500°C but disappear at 600°C showing complete decomposition of lignin. The inference to be drawn here is that the fibres contain low lignin content.

As shown in Figure 6, a distinct DTG peak, resulting mainly from the thermal decomposition of cellulose, is observed for all fibres. A visible difference between the three fibres tested (see Figure 6) is the height difference which is related to the rate of decomposition (Jin et al., 2013). The peak is highest for groundnut shell M1 followed by coconut shell M2 and the least is rice husk M1. This is an indication that the mass of decomposition per minute of groundnut shell M1 is highest for groundnut shell M1 than for coconut shell M2 and rice husk M1. This shows that groundnut shell M1 contains a higher proportion of cellulose than coconut shell M2 and rice husk M1. This is in line with the findings of Jin et al. (2013).

The decomposition characteristics of fibres are deduced from the various figures, and the activation energy calculated is presented in the next section and the results are summarised in Table 2. Parameter T_{onset} indicates an onset decomposition temperature of 269°C for groundnut shell M1, 290°C for coconut M2 and 284°C for rice husk M1. These values are divergent and indicate the effect of treatment paths on the onset of degradation. The two M1-treated fibres have almost the same (−4°C difference) onset of degradation, while M2-treated fibres show very low onset temperature degradation. Yao et al. (2008) reported that the onset of degradation for bagasse, bamboo, cotton stalk, hemp, jute, kenaf, rice husk, rice straw, wood-maple and wood-pine to be in the range of $215 \pm 10^\circ\text{C}$. Moreover, initial degradation of rice husk is found to be 229°C (Ndazi et al., 2007). These indicate that the treatment promotes increase in the onset of degradation with M1 being more beneficial than M2. Weight loss in this period (referred to W_{onset}) is observed to be 20% for groundnut shell M1, 34.2% for coconut shell M2 and 23.2% for rice husk M1. A higher value is noticed for M2 coconut fibres, indicating a higher initial rate of decomposition than groundnut and rice treated via M1. Decomposition at this temperature range shows the breakdown of amorphous hemicellulose materials. Higher decomposition at this point infers a higher content of hemicellulose in the fibres. This is in line with earlier findings using the DTG curve (see Figure 6). Parameter T_{max} presents

the maximum decomposition temperature of natural fibres as 349.5°C for groundnut shell M1, 335.9°C for coconut shell M2 and 355.6°C for rice husk M1. This indicates a higher degradation temperature for M1-treated fibres (groundnut shell M1 and rice husk M1), but a low degradation temperature for M2-treated fibres (coconut shell M2). The weight loss at this temperature, indicated by parameter W_f , is ~ 65% or higher for the fibres. The residual mass after decomposition is found to be 26.885% for groundnut shell M1, 24.5447% for coconut shell M2 and 30.612% for rice husk M1. This agrees with the studies of Jin et al. (2013) on the decomposition of various woods showing that wood with higher cellulose content gives lower residual mass than wood with lower cellulose content. This is an indication that rice husk M1 fibres contain less cellulose content than groundnut shell M1 and coconut shell M2 fibres.

Table 2 Thermal degradation parameters of processed fibres

S. No.	Fibres	T_{onset} (°C)	W_{onset} (%)	T_{max} (°C)	W_{max} (%)	W_f (%)	Activation energy (kJ/mol)	R^2
1.	Groundnut shell-M1	269.00	20.0	349.5	65.76	1.0591	105.936	0.9997
2	Coconut shell-M2	290.00	34.2	335.9	65.36	0.9778	78.238	0.9997
3	Rice husk-M1	284.00	23.2	355.6	67.34	1.1375	81.111	0.9995

The activation energies which measure the minimum energies involved in the sample decomposition are also used to assess the relative thermal stability of fibres due to treatments. The method of Broido (1969) is used in this study as given in equation (1). A detailed explanation of the theory and model is found in the published paper (Broido, 1969).

$$\ln(-\ln(1-X)) = -\frac{E}{RT} + \text{const.} \quad (1)$$

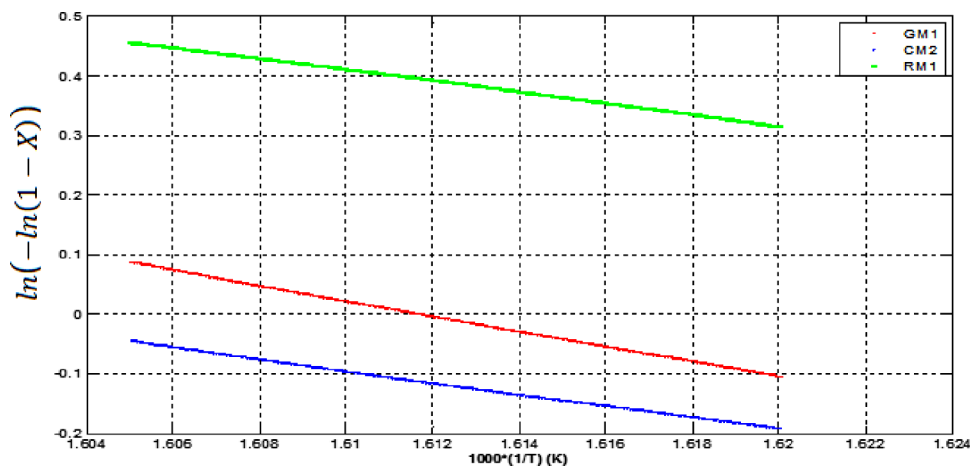
The plot of $\ln(-\ln(1-X))$ against $1/T$ should give a straight line whose slope is $-E/R$, where E is the activation energy of the degradation reaction (kJ/mol), R is the universal gas constant (8.314 J/mol K), T is the absolute temperature (K), X is the degree of decomposition given in equation (2) (Ahmad et al., 2012).

$$X = \frac{(w_0 - w_t)}{(w_0 - w_f)}, \quad (2)$$

where w_0 is the initial weight of the sample, w_t the actual weight of the sample at time t and w_f the final weight of the sample.

The plot (see Figure 8) of iso-conversional Broido model shows a general trend of activation energy. Activation energy of the fibres shows that groundnut shell M1 (105.936 kJ/mol.) required higher activation energy for decomposition than coconut shell M2 (78.238 kJ/mol.) and rice husk M1 (81.111 kJ/mol.). This has been attributed to the presence of susceptible hemicellulose and lignin in coconut shell M2 and rice husk M1 more than in groundnut shell M1. This confirm that M1-treated fibres are thermally stable than M2-treated fibres. This stability has been attributed to the effectiveness of the treatment in removing the amorphous portion from the surface of the fibres, making them useful as reinforcement in polymer composites.

Figure 8 Typical iso-conversional plot of Broido for processed fibres (see online version for colours)



5 Conclusion

In this study the following have been shown:

- The two processing paths used promote improvement in the thermal degradation behaviour of the fibres. Water adsorption capacity of the fibres improves as the amount of amorphous portion is greatly removed.
- For groundnut and palm bunch and stalk fibres, M2 treatment activates higher heats of dehydration than M1 treatment. This indicates that M1 treatment is effective in removing amorphous portion of the fibres compared to M2 treatment.
- For coconut shell and rice husk fibres, M1 treatment activates higher heat of dehydration than M2 treatment, showing that M1-treated fibres contain more amorphous portion than M2-treated fibres.
- The treatment promotes increase in the onset of degradation with M1 being more beneficial than M2.
- The maximum decomposition temperature for processed fibres is 349.5°C for groundnut shell M1, 335.9°C for coconut shell M2 and 355.6°C for rice husk M1.
- Highest activation energy is shown by groundnut shell M1 (105.936 kJ/mol.) followed by coconut shell M2 (78.238 kJ/mol.) and rice husk M1 (81.111 kJ/mol.).

Acknowledgements

The authors acknowledge with grateful thanks the provision of facilities by the Soochow University, China, the technical assistance of Messrs Sun Jun and Xinbo Wang of the School of Materials Science and the support of the University of Lagos, Nigeria.

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