CHARACTERISATION OF THE MECHANICAL AND THERMAL DEGRADATION BEHAVIOUR OF NATURAL FIBRES FOR LIGHTWEIGHT AUTOMOTIVE APPLICATIONS

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Abstract

It is well established that light-weighting of automotive parts leads to reduced carbon emissions over vehicle lifetime. Mineral fibres and fillers have a relatively high density and may require high levels of energy in their production, resulting in a large carbon footprint. Natural fibres have been identified as a potential candidate to substitute mineral fillers in automotive application of thermoplastic matrix composites. This paper focuses on the characterisation of the mechanical and thermal degradation of two types of natural fibres (date palm and coir fibres) as part of an evaluation of their potential for the substitution of high density mineral fillers with more environmentally friendly lower density natural fibre reinforcements.

1 Introduction

In the past few years, the light-weighting of automotive parts has catalysed strong growth in automotive application of thermoplastic matrix composites, which possess both higher performance and mass processability.
Nevertheless, the use of these mineral fillers has inherent pitfalls, they have a relatively high density and can require very high levels of energy in their productions, resulting in a large carbon footprint. In this context, a significant body of evidence is being amassed, which suggests that natural fibres may have potential to compete with mineral fibres and fillers as a more environmentally friendly reinforcement [1][2]. Their adoption could lead to lower energy consumption during the vehicle's overall life, due to reduced production energy, light-weight products (therefore a fuel-saving strategy) and increased use of renewable resources. However, commercial reality requires a minimum level of cost-performance-processability balance from such fibres.
One of the main issues in the processing of natural fibres is their degradation at high temperatures. Consequently, the upper temperature during processing in composites needs to be limited. The range of temperatures for the thermal degradation of the main components of natural fibres has been identified for higher temperatures in comparison to normal processing temperatures [3][4]. In any case, due to the proximity of the degradation and processing temperatures, it seems necessary to precisely characterise the onset temperatures of the degradation process and the influence on the fibre's mechanical performance. Results will be presented from single fibre tensile testing of non-treated and heat-treated fibres for characterisation of fibre modulus, strength and failure strain along with thermal degradation studies.

2 Materials

The two types of fibres chosen for this study are date palm and coir fibres, both provided by Sabic.

3 Experimental

3.1 Thermal Volatilisation Analysis

The thermal degradation behaviour of date palm and coir fibres has been characterised through Thermal Volatilisation Analysis (TVA). The TVA analyses were carried out in a built in-house TVA line, based on the techniques and device described by McNeill et al.[5]. The system is made up by a sample chamber, connected in series to a primary liquid

nitrogen cooled sub-ambient trap and right after a set of four secondary liquid nitrogen cooled cold traps. The entire system is continuously pumped to a vacuum of 10^{-4} Torr by two pumps: a two stage rotary pump and oil diffusion pumping system. The condensable volatiles could be initially trapped at two points: The cold-ring and the primary sub-ambient trap. The cold-ring is water cooled (Temperature of approximately 12 ºC) and is right above the heated area of the sample tube. The primary sub-ambient trap is liquid nitrogen cooled (Temperature of approximately -196 ºC) and is designed for capturing all the lower boiling point volatiles. In order to monitor the evolution of condensable and non-condensable volatiles as a function of pressure vs. temperature and time, two linear response Pirani gauges were located at the entrance and exit of the primary sub-ambient trap. The linear response Pirani gauges provide a precise pressure measurement, necessary for the pressure peak integration; where the different areas of the curve are associated with the quantity of evolved volatiles. The low boiling species that have been trapped in the primary sub-ambient trap could be distilled into separate secondary cold traps by slowly heating the primary sub-ambient trap to ambient temperature. The separated fractions could be subsequently removed into gas-phase cells for Fourier transform infrared spectroscopy (FTIR) analysis.

The TVA runs were carried out under vacuum, with a heating rate of 10 ºC·min^{-1} to a maximum temperature of 550 ºC. A Hiden HPR-20 QIC sampled a continuous product stream during the degradation (1-100 amu) and differential distillation (1-250 amu) runs. The sub-ambient differential distillation of collected volatiles was carried out by heating the primary sub-ambient trap from -196 ºC to room temperature. Coir's volatiles were separated into four major fractions, while palm's were separated into three. All the volatiles were then analysed through FTIR.

All FTIR analysis of the collected TVA products were carried out using a PerkinElmer Spectrum 100 used in transmission mode.

3.2 Thermogravimetric analysis

A NETSZCH STA 449 F1 Jupiter was used to analyse the thermal stability of date palm fibre. The TGA analyses were carried out under nitrogen atmosphere in two different configurations. In the first run, the heating profile was established as: initial ramp, isothermal degradation and cooling ramp. The initial ramp was defined with a heating rate of 10 ^{0}C·min^{-1} and the isothermal degradation was established at 550 °C. The first run had a heating profile equivalent to the TVA's.

The second configuration was defined as two consecutive ramps, followed by isothermal degradations. Both ramps had a heating rate of 10 ^{0}C·min^{-1} while the isothermal degradation was established at 200 °C and 300 °C. The critical temperature of 200 °C was chosen based on the temperature at which the first stages of degradation normally occur.

3.3 Heat treatment of fibres and observation

The heat treatment of fibres was carried out in order to accomplish two main goals. The first and most important was to provide conditioned fibres for later tensile testing. The secondary aim was to analyse the diameter and surface of the fibres before and after the heat treatment.

The conditions of the heat treatment of fibres addressed for tensile testing were established around the normal temperatures for processing reinforced polypropylene, which coincide with the temperatures where the initial degradation is observed. The treatments were defined as the combination of three different temperatures (180, 200 and 220 ºC) and two different times of treatment (10 and 30 minutes).

All the fibres were individually separated until no fraying could be seen with the naked eye. Subsequently, they were placed in an aluminium tray for the heat treatment. The heat treatments were carried out in an oven Nabertherm P-330. The samples were introduced in the oven and then heated up to the temperature of the treatment in a period of 20 minutes. The temperature was then kept constant for the length of the treatment. Afterwards, the samples were taken off the oven and cooled down at room temperature.

Fibres addressed to diameter and surface observation, were also individually separated until no fraying could be seen with the naked eye. Then, they were positioned on a glass slide, as it is illustrated in Fig. 1 fixing them to the glass with the help of double side tape and bulldog clips. Before the heat

treatment, a picture was taken of the middle point of the gauge length, under transverse observation, using a Leica microscope at 10x magnification. Afterwards, fibres mounted on to the glass slide were heat treated in the oven following the same heating process as the 220 °C and 30 min profile given for fibres addressed to tensile testing. Subsequently, fibres were again photographed at approximately the same point as before. Finally, in each picture, the diameter was measured at three different points along the fibre. The final value for the diameter was taken as the average of these three measurements.

After the diameter measurements, the surface of fibres was observed using a Field Emission Scanning Electron Microscope (FE-SEM) HITACHI SU-6600.

3.4 Tensile Test

The tensile testing was designed as a set of experiments that analysed the mechanical properties of date palm and coir fibres before and after certain heat-treatments. For each different condition, 30 fibres were tested.

The fibres (non-treated and treated) were mounted for testing on card frames made from 250 g/m^2 card. The gauge length used for testing was 20 mm. LoctiteTM Gel Superglue was used to fix the fibres to the card. All fibres were photographed at the middle point of the gauge length under transverse observation using a Leica microscope at 10x magnification. The three most representative diameters in each picture were measured using the software ImageJ. The fibre diameter was estimated as the average of these three measurements. Tensile testing was carried out using an Instron 3342 tensile testing machine with a 100 N load cell at 5% strain per minute. For the tensile test, card and fibre were clamped up to the gauge length in order to avoid any slippage.

4 Results and Discussion

4.1 TVA analysis of date palm and coir fibre

The thermal degradation of date palm and coir fibres under vacuum produced, for both cases, a significantly higher amount of condensable volatiles compared with the produced non-condensable. The TVA plots, showing the evolution of the volatiles vs. temperature and time for each fibre, are illustrated in Fig. 2. The onset degradation temperatures, the evolution rate peak maxima and the relative amount of condensable and non-condensable volatiles are summarised in Table 1. The relative amounts of volatiles have been calculated through the integration of the pressure vs. time curves.

From Fig. 2 and Table 1 it can be observed that both fibres have a similar degradation profile, with a main degradation peak at a temperature of approximately 357 ^{0}C. The shape of the degradation profile is defined by a main peak, preceded by a big shoulder – at a temperature of approximately 300 ^{0}C – and followed by a smaller broad shoulder.

The onset degradation temperature was defined as the point at which the system's pressure reaches $7{\cdot}10^{-5}$ torr. These temperatures were almost identical for both fibres, being 196 ^{0}C for date palm and 200 ^{0}C for coir. Therefore the thermal stability of both fibres could be considered as equal.

Both fibres evolved a significant amount of non-condensable volatiles as illustrated in Fig. 2 and Table 1, representing a 23% and 25 % of the total of volatiles, for date palm and coir respectively.

Collected volatiles for both fibres were separated by sub-ambient distillation. The differential distillation graphs and distillation fractions - coir Cf and date palm Pf - for each fibre are represented in Fig. 3. The individual peaks represent discrete components of the total volume of collected volatiles. Peaks were numbered from 1 to 3, with an additional point 4. The pressure profile during distillation is almost identical for the two different fibres, and therefore the degradation products were expected to be extremely similar. The only significant difference is visible in point number 4 – which main component was water –, where in the case of date palm, the increment in pressure is not detected. The main component of each peak was identified by online mass spectrometry and FTIR as: 1- CO_2, 2- Formaldehyde and 3-water. The mass spectrometry results for peak 1 and the FTIR of the fraction 2 (Pf2) of the date palm study are shown in Fig. 4 and Fig. 5 as an example of the analysis techniques used. Peak 3 is the main volatile product of degradation. Traces of other volatiles were also identified: methanol, ketenes, acetic acid and long aliphatic fragments from unknown long hydrocarbon molecules. The results are in good agreement with the studies on pyrolytic degradation of cellulose [6–8].

This thermal degradation analysis represents general study of the degradation process in the conditions of injection moulding of PP. Due to the high temperatures achieved during the analysis, the degradation of the fibres is high. Therefore, the amount of fragments - especially long aliphatic compounds - from low temperature degradation products is high, making difficult to trace back the initial degradation products. In this respect and as a precise analysis of the injection moulding temperature's range, it seems necessary to run an isothermal degradation on the onset temperatures for both fibres to precisely characterise the degradation mechanisms and degradation products at these points.

Fig. 6 shows a date palm fibre – after TVA degradation – SEM micrograph. It can be appreciated how the cells' external walls have collapsed, and how a major part of the cells' internal wall is gone. The structural degradation pattern is in good agreement with the degradation of the three main components of natural fibres: cellulose, hemicellulose and lignin. Each individual cell is formed by a series of layers. The internal layers are the ones to provide rigidity to the cell and therefore they are mainly made up by cellulose and hemicellulose and other organic components [9]. In the external layers the abundance of lignin is much higher than in the internal layers. Lignin is the most thermally resistant of the main three components [3][10], above cellulose and hemicellulose- the least stable. Therefore the remaining structure of the fibre, after the thermal degradation, will be made up by the cells' external walls, as can be observed in Fig. 6.

4.2 TGA of date palm fibre

TGA was used in this study to further analyse the non-oxidative thermal stability of date palm fibre. Fig. 7 and Fig. 8 show the mass loss of the two degradation studies. In the first study, Fig. 7, three well known processes [3] can be differentiated: 1. The initial loss- temperatures lower than 150 ^{0}C - can be attributed to the loss of water , 2. The second process – temperatures from 150 to 300 ^{0}C- to the degradation of hemicellulose and 3. The third process – temperatures higher than 300 ^{0}C – is attributed to the degradation of cellulose.

In the second study, the two isothermal degradations confirmed the existence of degradation at a relatively low temperature of 200 °C. Between the initial point and the final point of the first isothermal there was a mass loss of approximately 1.5 %. The results are in good agreement with similar studies on coir fibre [11], which further highlight the similarities between coir and date palm observed in the TVA studies.

4.3 Fibre observation

Fig. 9 compares the value of diameter before and after the heat treatment for both fibres. It is well known that the precise measurement of the cross section area is essential to precisely characterise the mechanical properties of natural fibres [12], however, due to the comparative nature of the study, transverse observation was chosen for practical reasons. From the equation of the least squares fitted lines, it can be observed how the diameter – based on transverse observation – slightly decreased. Due to the variability of the cross section area of natural fibres and to the fact that the pictures were not taken in the exact same point, there is certain scattering in the data. The slight reduction of the cross section area provides evidences of a structural degradation that was also observed, to a higher extent, after high temperature non-oxidative thermal degradation, Fig. 6.

Fig. 10 shows four different fibres that have been selected as representative of each group. The fibres on the left are non-treated fibres while the ones on the right were heat treated. In terms of the surface, no significant differences could be observed apart from a consistent slight shrinkage of the external walls of the fibres.

4.4 Tensile testing

A full analysis of the data is shown in Table 2. Fig. 11 and Fig. 12 show the tensile strength of coir and date palm fibres. In both cases, there is a dramatic drop in the tensile strength of heat treated fibres. The length of the treatment has as well a clear influence. Any 10 min. heat treatment reduced the tensile strength less than its 30 min. equivalent. In Fig. 12 it can be seen how, for the case of 10 min. treatment, the tensile strength of date palm is approximately constant until the temperature reaches 220 ^{0}C. It is not the same case for coir fibre, where the degradation in tensile strength is observed in all treatments. Fig. 13 compares the behaviour of both fibres after the 30 min. treatments, showing how the

tensile strength of both fibres starts to fit the same trend-line for high temperatures.

Fig. 14 shows the failure strain of both fibres for all heat treatments. Strain at break dramatically drops after any heat treatment. As it was observed in the tensile data the higher the temperature and time the higher the degradation.

Young's modulus data doesn't follow the same trend as tensile strength and strain at break. Fig. 15 and Fig. 16 show Young's modulus of coir and date palm for each different heat treatment. For both fibres, it can be appreciated how the modulus either remains approximately constant or slightly increases in comparison with non-treated fibre's modulus.

Coir and date palm are natural fibres with a high cellulose microfibril angle (MFA) and therefore their stress-strain curves have two differentiated phases [9][13]. The initial part of the curve is almost a linear elastic stress-strain curve. The second phase – with much higher strain – is considered to be a non-elastic and non-linear region. Young's modulus, for this type of fibres, is measured in the initial part [13] – initial modulus. As it can be seen in Fig. 15 and Fig. 16, Young's modulus remains almost constant – or slightly increase- while the tensile strength and failure strain drop, therefore the thermal degradation process is mainly affecting the secondary phase of the stress-strain curve. The highest temperature that any of the treatments reached is 220 ^{0}C, which is within the range of the thermal degradation of hemicelluloses [10]. Hemicelluloses are considered to be a component of the matrix of the secondary cell walls, where the cellulose fibres are embedded[9]. Therefore their degradation is in direct relation to strain to failure and consequently with the tensile strength. Fibres' Young's modulus does not drop due to the fact that the range of temperatures for the degradation of cellulose – main contributor to the rigidity of the fibres - is in between 300 to 400 ^{0}C[3][4].

5 Conclusions

This work has shown how important is to control the processing conditions of coir and date palm due to the observed thermal degradation. The non-oxidative degradation studies – TVA and TGA- have demonstrated how the onset degradation temperature is approximately 200 ^{0}C. The direct observation of fibres and the analysis of the tensile data showed how the thermal degradation affects the structural integrity and mechanical properties of the fibres. The mechanical testing of treated and non-treated fibres has shown how there is a dramatic drop in the tensile strength and failure strain when processing temperatures rise above 200 ^{0}C, as well as a clear time dependence of the degradation.

Acknowledgements

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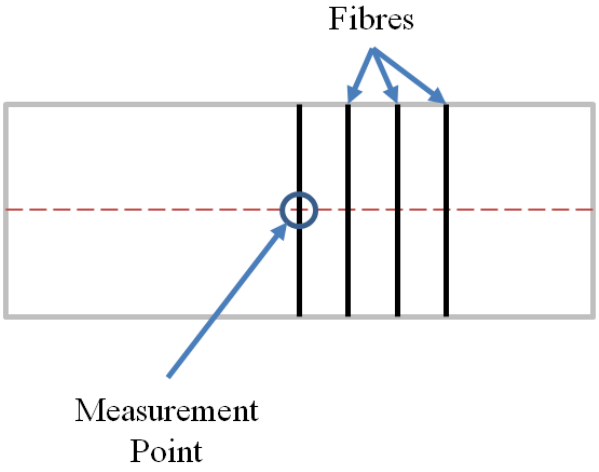

Fig. 1 Sample preparation for diameter and surface observation of heat treated fibres.

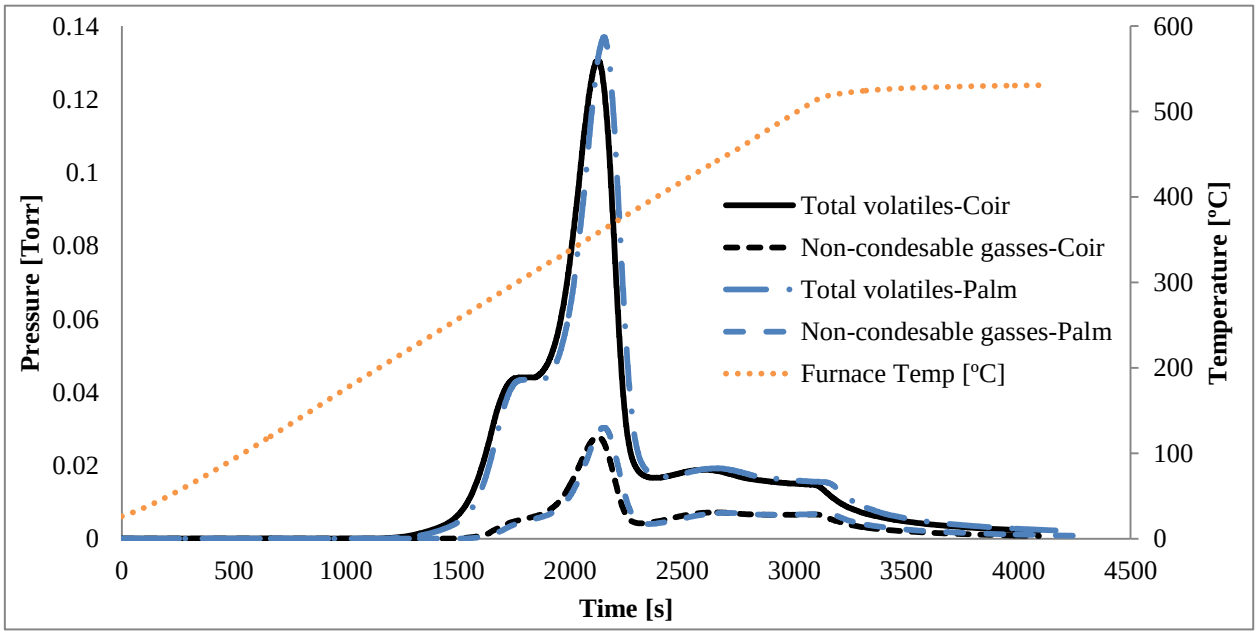

Fig. 2. TVA plots of the degradation of coir and date palm fibres showing the rate of volatiles as a function of pressure vs. the furnace temperature.

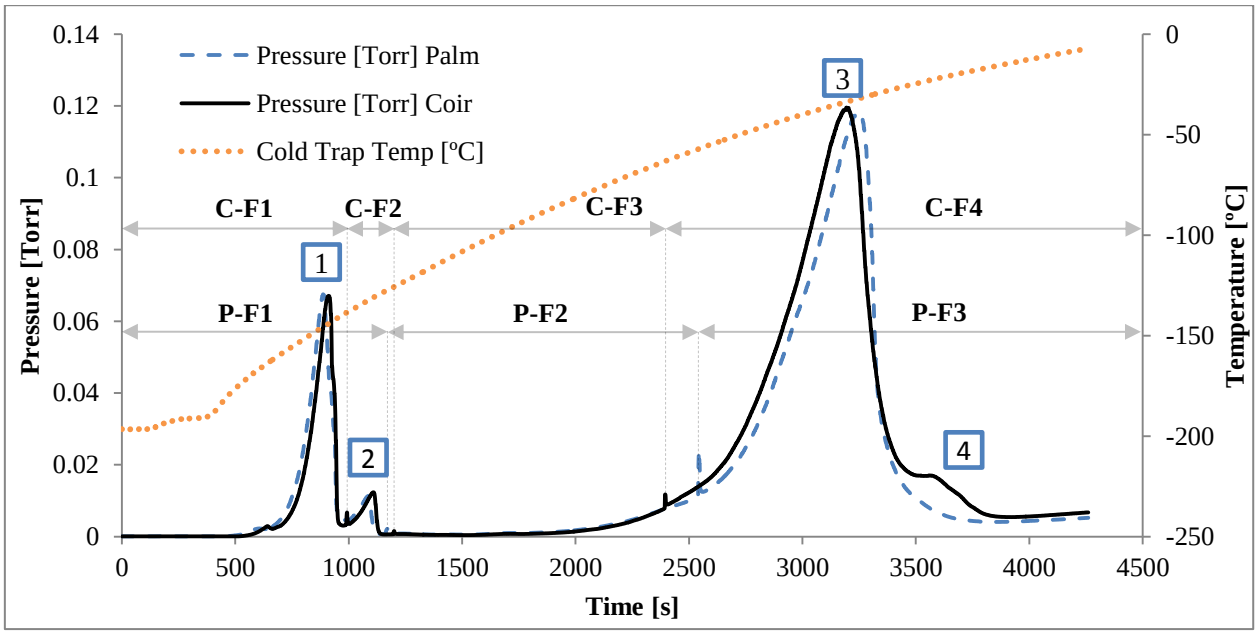

Fig. 3. Differential distillation plots of coir and date palm fibres.

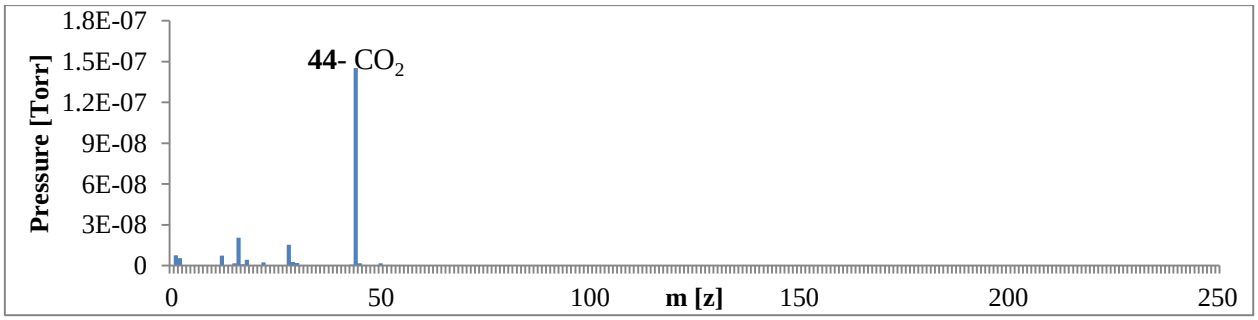

Fig. 4. Mass spectrum of the point 1 from date palm degradation having a main peak at 44 amu corresponding to CO_2.

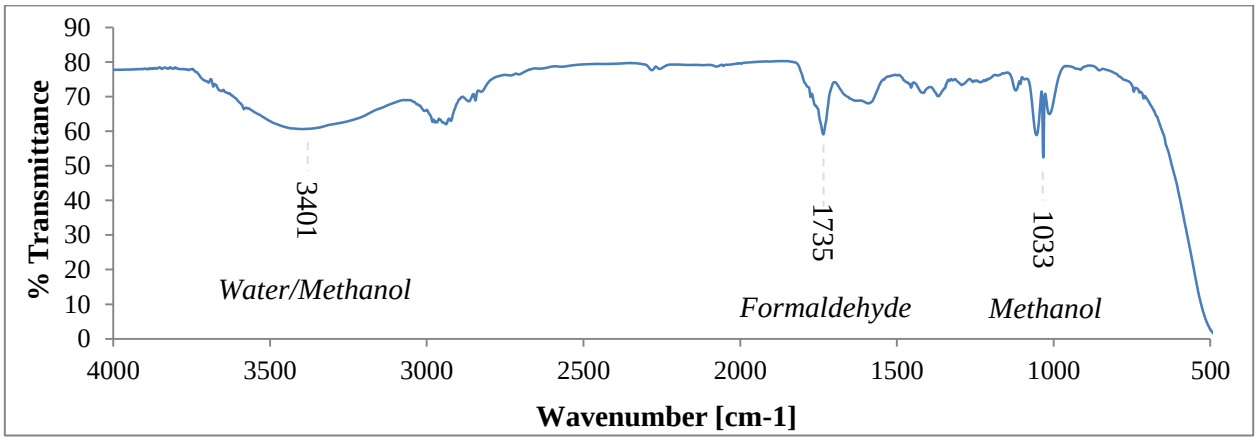

Fig. 5. FTIR spectra of the collected fraction 2 from date palm degradation.

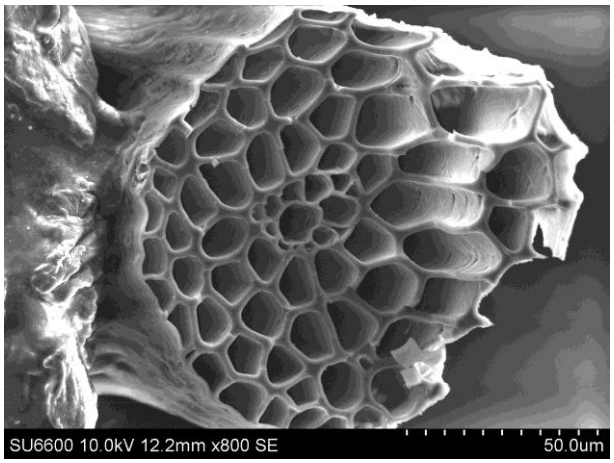

Fig. 6. SEM, date palm fibre after TVA.

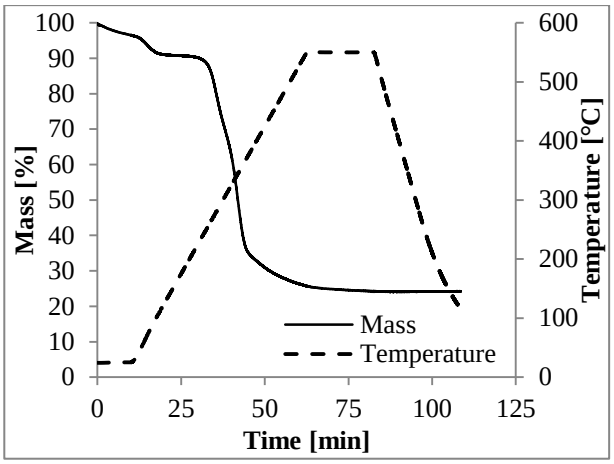

Fig. 7. TGA mass loss curve I for date palm fibre.

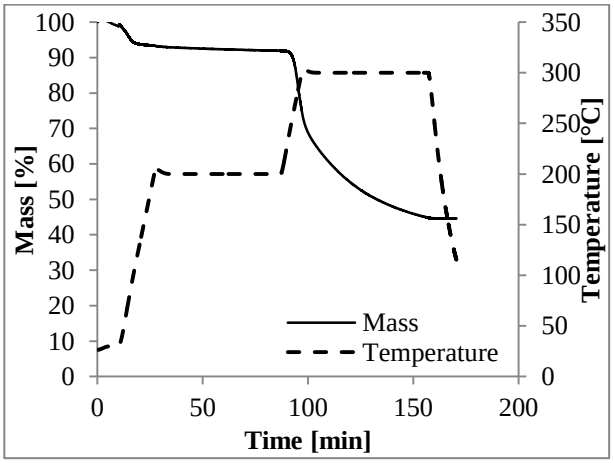

Fig. 8. TGA mass loss curve II for date palm fibre.

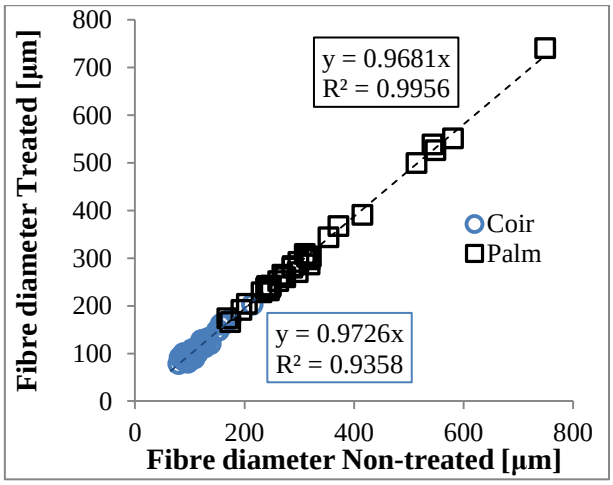

Fig. 9. Non-treated fibre diameter vs. Treated fibre diameter.

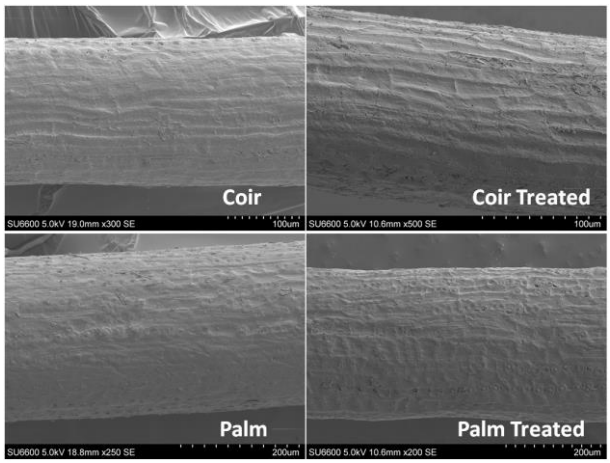

Fig. 10. SEM surface observation of treated and non-treated fibres.

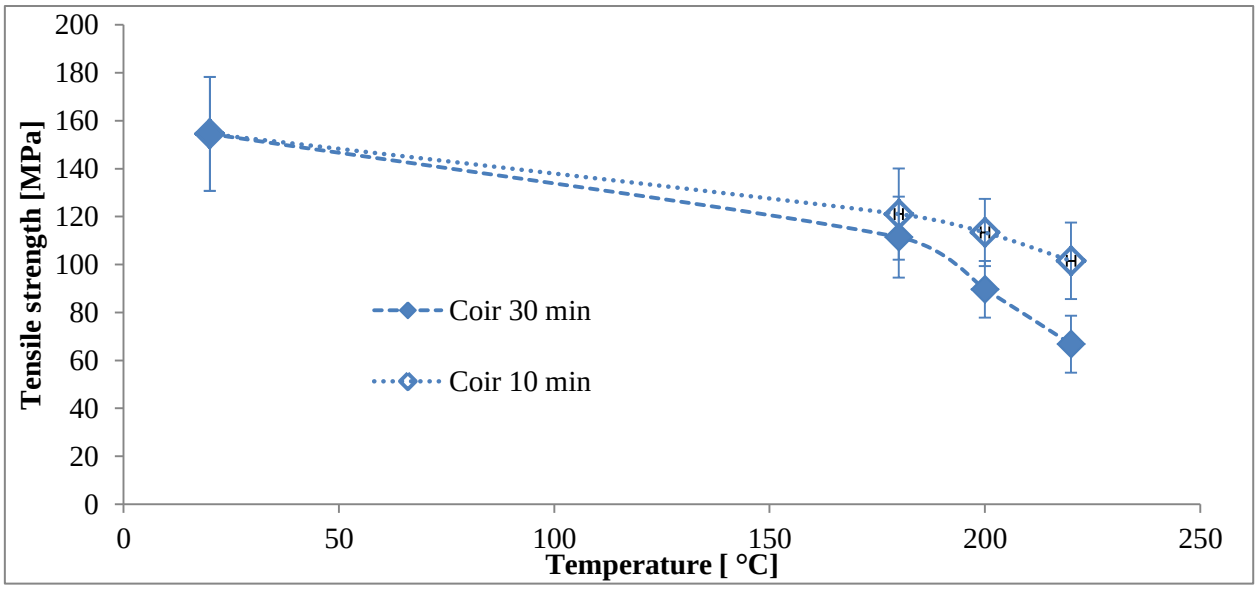

Fig. 11. Tensile strength of coir fibre vs. temperature for 30 and 10 min. heat treatments.

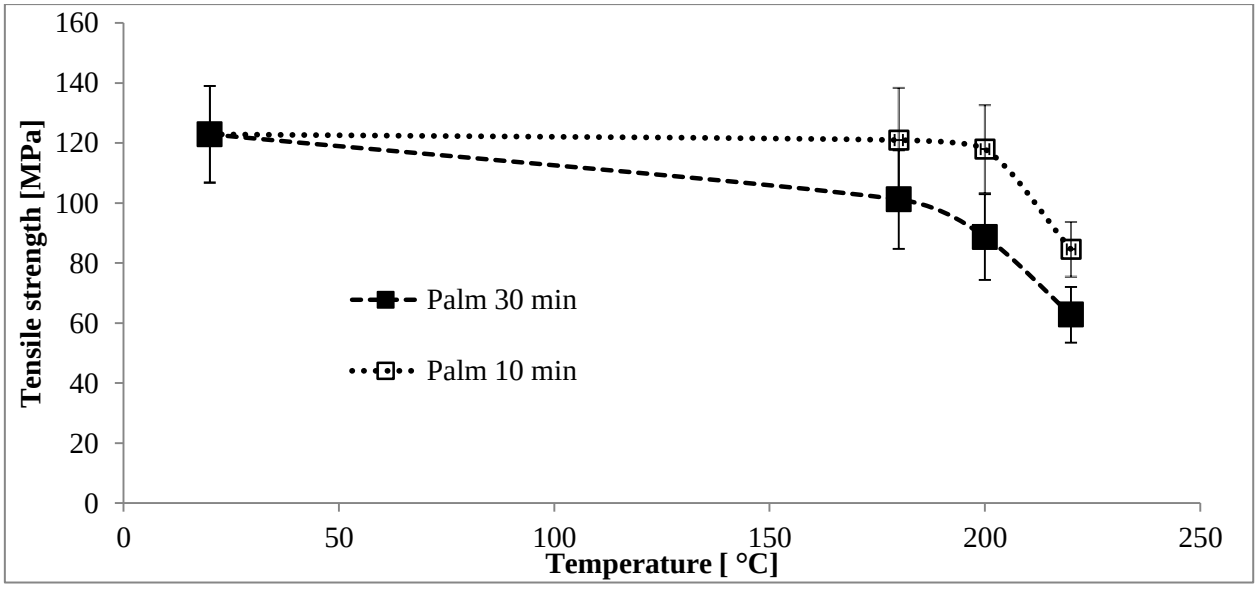

Fig. 12. Tensile strength of date palm fibre vs. temperature for 30 and 10 min. heat treatments.

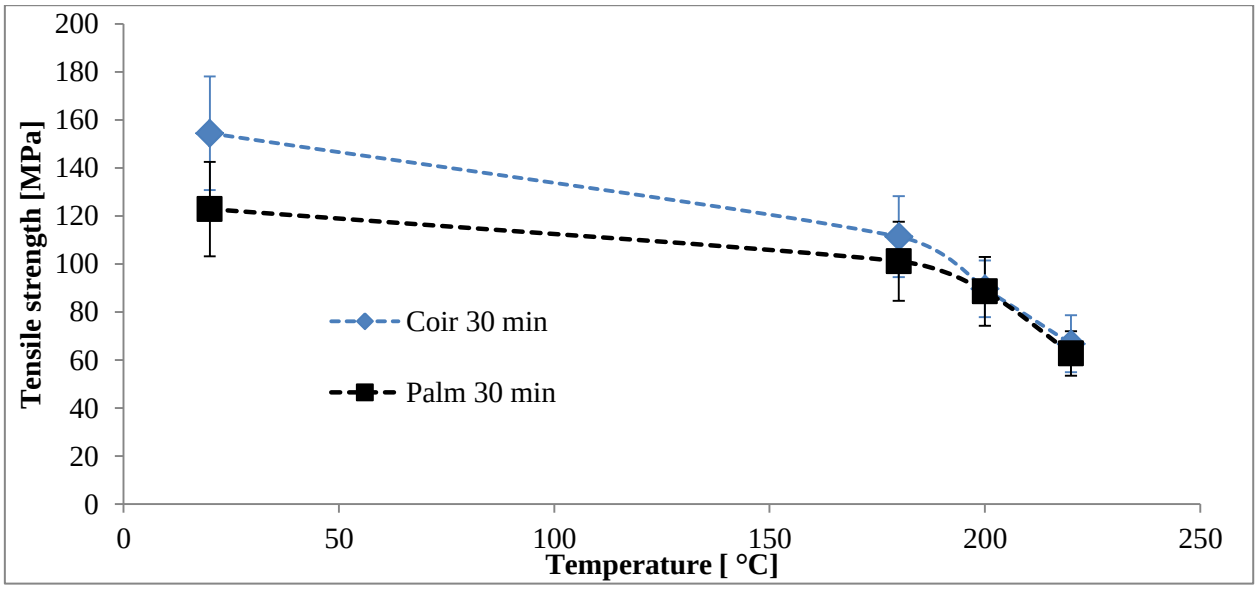

Fig. 13. Tensile strength of date palm and coir fibre vs. temperature for 30 min. heat treatment.

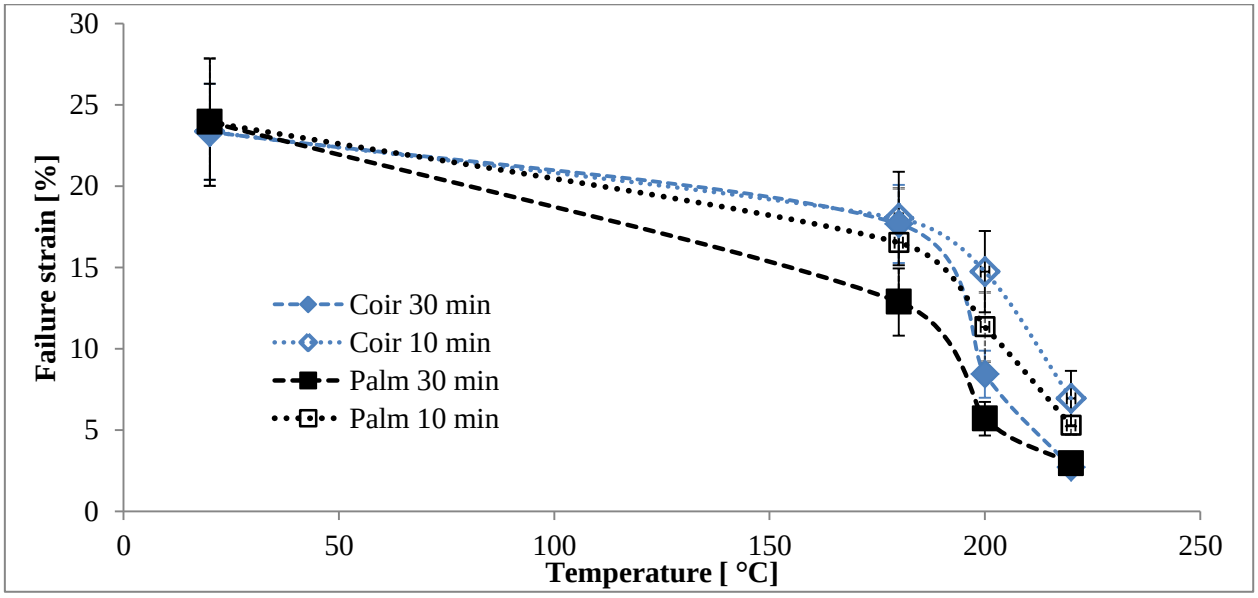

Fig. 14. Strain to failure of date palm and coir fibre vs. temperature for 30 and 10 min heat treatment.

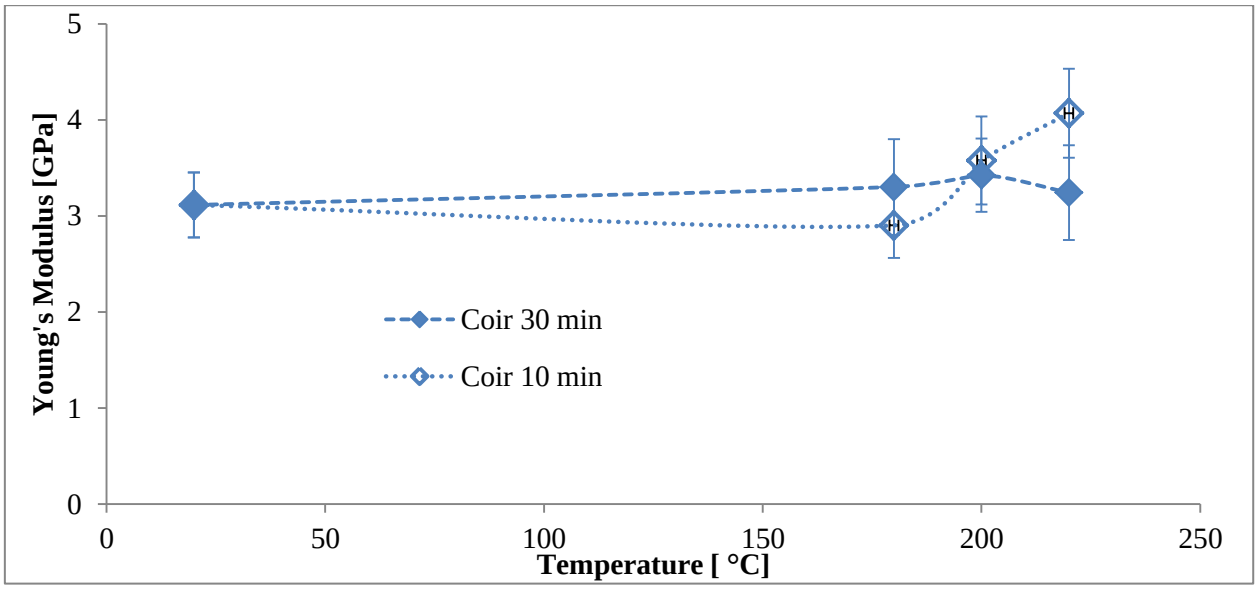

Fig. 15. Young's modulus of coir fibre vs. temperature for 30 and 10 min. heat treatments.

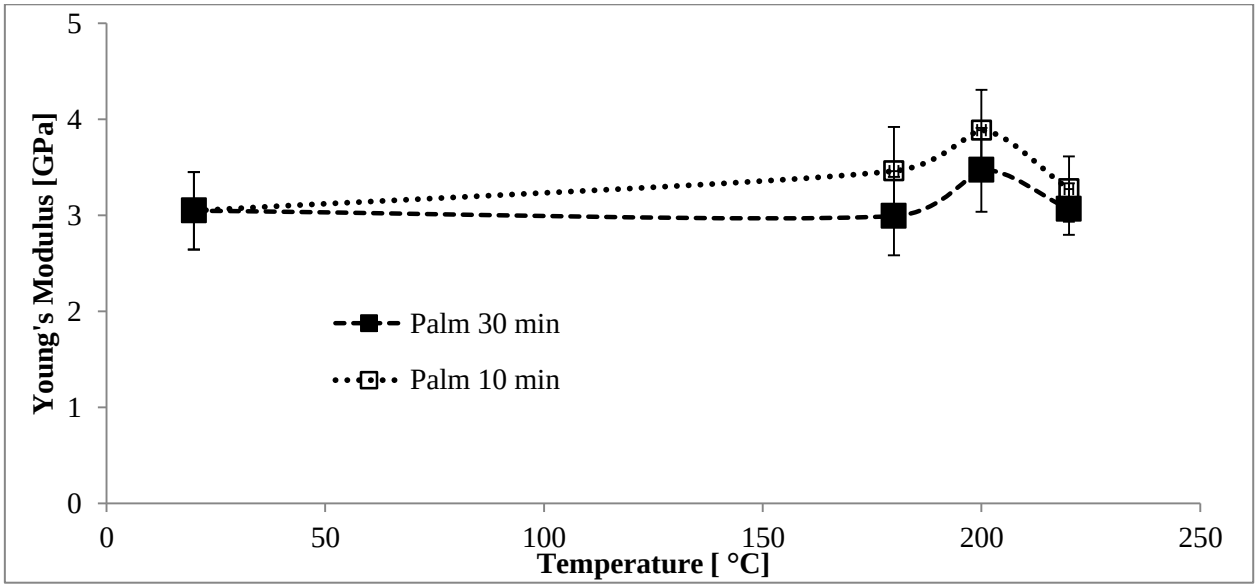

Fig. 16. Young's modulus of date palm fibre vs. temperature for 30 and 10 min. heat treatments.

Table 1. Onset degradation temperatures, maximum volatile evolution rate peak temperatures, overall level of evolved volatiles and overall level of non-condensable volatiles. Data from Fig. 2: TVA plots.

Fibre	**Onset degradation temperature [^{0}C]**	**Max. evolution rate: Peak temperature [^{0}C]**	**$\int P_{condensable}(T)$ [Torr s]**	**$\int P_{non\text{-}condensable}(T)$ [Torr s]**
Coir	200	358	64	16
Date palm	197	357	65	15

Table 2. Tensile properties of single natural fibres

Sample	Young's modulus [GPa]		Tensile strength [MPa]		Failure strain [%]		Diameter [μm]	
	Mean	95% Confidence limits	Mean	95% Confidence limits	Mean	95% Confidence limits	Mean	95% Confidence limits
Coir Untreated	**3.1**	**0.3**	**154.5**	**23.7**	**23.3**	**3.0**	**199**	**31**
Coir 180 ^{0}C, 10 min	2.9	0.3	121.1	19.0	18.0	2.9	166	14
Coir 200 ^{0}C, 10 min	3.6	0.5	113.4	14.0	14.7	2.5	152	17
Coir 220 ^{0}C, 10 min	4.1	0.5	101.5	15.9	6.9	1.7	150	19
Coir 180 ^{0}C, 30 min	3.2	0.5	111.4	16.9	17.7	2.4	149	14
Coir 200 ^{0}C, 30 min	3.4	0.4	89.7	11.8	8.4	1.4	177	21
Coir 220 ^{0}C, 30 min	3.3	0.5	66.8	11.9	2.7	0.4	181	24
Date palm Untreated	**3.0**	**0.4**	**122.9**	**19.6**	**23.9**	**3.9**	**223**	**43**
Date palm 180 ^{0}C, 10 min	3.5	0.5	121.0	17.4	16.5	3.3	292	67
Date palm 200 ^{0}C, 10 min	3.9	0.4	118.0	14.7	11.3	2.1	239	46
Date palm 220 ^{0}C, 10 min	3.3	0.3	84.6	9.2	5.3	0.6	299	56
Date palm 180 ^{0}C, 30 min	3.0	0.4	101.2	16.4	12.9	2.1	246	34
Date palm 200 ^{0}C, 30 min	3.5	0.4	88.6	14.3	5.7	1.0	266	52
Date palm 220 ^{0}C, 30 min	3.1	0.3	62.7	9.3	2.9	0.6	258	52