

Thermal degradation behaviour of natural fibres at thermoplastic composite processing temperatures

James L. Thomason* and Jose L. Rudeiros-Fernández

University of Strathclyde, Department of Mechanical and Aerospace Engineering, 75 Montrose Street, Glasgow G1 1XJ, United Kingdom.

*Corresponding Author, james.thomason@strath.ac.uk, Tel:0044-141-5482691

Abstract

Natural fibres have been identified as a potential substitute for mineral fillers in thermoplastic matrix composites for automotive applications. However, natural fibres are known to be susceptible to thermal degradation at relatively low temperatures. This paper focuses on the characterisation of the thermal and mechanical degradation of date palm and coir fibres as part of an evaluation of their potential as a reinforcement for polypropylene composites. The thermal degradation of the fibres and the resultant volatiles produced have been analysed for a range of typical polypropylene processing temperatures. The effect of the thermal degradation of the fibres on their mechanical performance has also been evaluated using single fibre tensile testing. The results indicate that processing temperatures should be minimised as much as possible and certainly kept below 200 °C.

Keywords: Natural fibres, Thermal degradation, thermoplastic composites, Thermal analysis, Fibre strength

1. Introduction

The automotive industry is increasingly implementing light-weighting strategies in the design of automotive components in order to reduce carbon emissions over vehicle lifetime. In this respect, the use of fibre and filler reinforced thermoplastic composites have played a major role. Much of the success in this area has been due to improvements in fundamentally understanding the influence of fibre content, fibre diameter, fibre length and fibre-matrix adhesion in the composite. Nevertheless, the relatively high density and high levels of energy required in the production of composites based on man-made fibres may possibly have left room for natural fibres to compete in certain applications. It is thought that natural fibres may offer a viable replacement as a renewable and environmentally friendly reinforcement with an overall reduced carbon footprint. It has been reported that natural fibres may have the potential to compete with mineral fibres and fillers in certain areas [1,2]. Their adoption could lead to lower energy consumption over vehicle life, due to reduced production energy, light-weight products (with fuel-saving benefits) and increased use of renewable resources.

In this regard, one of the main issues in the processing of natural fibres is their potential degradation at high temperatures [2,3]. When these lignocellulosic fibres are heated in the range of 100 to 250 °C, physical and chemical changes in their properties have been observed due to processes such as depolymerisation, oxidation, hydrolysis, dehydration, decarboxylation and recrystallization [2-4]. The thermal behaviour of natural fibres can be analysed by the degradation of their individual main components (i.e. cellulose, hemicellulose and lignin). This thermal degradation is also different depending on the type of atmosphere (i.e. inert or oxidative atmosphere). Stamm [5] pointed out that the degradation of natural fibre is greater in the presence of air than in its absence, because of oxidation by atmospheric oxygen. Schwenker and Pacsu [6] showed that cellulose decomposes under an

[Type here]

inert atmosphere, into a complex mixture of organic acids, aldehydes, ketones, water and levoglucosan. In a later study, Roberts [7] pointed out that the decomposition of hemicellulose mainly takes places between 200 and 260 °C, followed by cellulose at 240 to 350 °C and lignin at temperatures between 280 to 500 °C. Cellulose, hemicellulose and lignin have quite different reaction kinetics, hemicellulose being the most reactive and lignin the least. Asim *et al* recently reviewed the thermal stability of natural fibres and their polymer composites and confirmed that the thermal degradation of natural fibres is still a pressing issue [3]. They also noted that the thermal degradation of natural fibres correlates closely to the degradation of their main chemical constituents. They further observed that natural fibre-reinforced composites exhibit better thermal stability than the fibres alone.

The range of temperatures for the thermal degradation of the main components of natural fibres has been identified within the range of temperatures used in standard thermoplastic moulding processing [8,9]. Thermal degradation influences the reinforcing performance of natural fibres, generally negatively, and it is crucial to understand their behaviour at composite processing temperature conditions. It has been shown that thermal degradation of natural fibres can lead to a decrease of their mechanical properties, but also to poor organoleptic properties such as odour and colour [2,8,9]. Van de Velde and Baetens [10] investigated the thermal and mechanical properties of flax fibres. They recognised that natural fibres are subject to degradation under the influence of temperature. Even at relatively low temperatures (120 °C), after two hours, fibre elongation at break significantly decreased. Exposure to higher temperatures led to faster degradation than for lower temperatures. Gassan and Bledzki [4] analysed the thermal degradation of flax and jute fibres and observed significant reduction in the tenacity of fibres, which was clearly time dependent, for treatments at 210 °C. Polypropylene (PP) is a thermoplastic composite matrix polymer of

[Type here]

high interest in automotive applications [11,12]. However, processing temperatures for PP based composites must clearly be well above the PP melting temperature of 165 °C and lie typically in the 200-230 °C range. Consequently, the production of reliable natural fibre reinforced PP composite parts requires an in-depth understanding of the degradation of the fibres at the required processing temperatures.

We have been studying the potential of coir and palm leaf fibres as a reinforcement for polypropylene based moulding compounds for use in automotive applications [11]. Such applications normally require two high temperature processing steps, one for forming a fibre-polymer intermediate compound and the second for processing such a compound into the final part. Typical examples are extrusion and injection of short fibre reinforced PP and compounding and moulding of long fibre reinforced PP [12]. This paper presents results of the investigation of thermal degradation of coir and palm fibres at PP processing temperatures. Results are presented from thermal degradation studies and analysis of thermal degradation products along with single fibre tensile testing of heat-treated fibres for characterisation of fibre modulus, strength and failure strain.

2. Experimental

2.1 Materials

Date palm and coir fibres were both provided by the industrial sponsor SABIC Petrochemicals B.V. (The Netherlands), but further information on the origin and extraction method of these fibres is not known.

2.2 Thermogravimetric analysis

[Type here]

A TA instruments Q50 TGA was used to analyse the thermal stability of the date palm and coir fibres. In a first set of experiments, thermogravimetric analysis (TGA) was carried out under both nitrogen and air gas flow (60 ml min^{-1}) using a simple dynamic heating rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ up to a maximum temperature at $600 \text{ }^{\circ}\text{C}$. In a second set of experiments TGA was carried out in air atmosphere with an initial temperature ramp at $10 \text{ }^{\circ}\text{C min}^{-1}$ up to an isothermal degradation temperature of either 180 , 200 or $220 \text{ }^{\circ}\text{C}$. Fibres were tested as received.

2.3 Thermal Volatilisation Analysis

Chemical analysis of the thermal degradation behaviour of date palm and coir fibres was characterised using Thermal Volatilisation Analysis (TVA). TVA was carried out using an in-house built TVA line (see Figure 1) based on the techniques and devices described by McNeill *et al* [13]. The system was made up of 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 was continuously pumped to a vacuum of 10^{-4} Torr by two pumps: a two stage rotary pump and an 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 was water cooled (at a temperature of approximately $12 \text{ }^{\circ}\text{C}$) and was positioned directly above the heated area of the sample tube.

The primary sub-ambient trap was liquid nitrogen cooled and was designed to capture all the lower boiling point volatiles. In order to monitor the evolution of condensable and non-condensable volatiles as a function of pressure versus 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 were 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 were 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 $10\text{ }^{\circ}\text{C min}^{-1}$ to a maximum temperature of $550\text{ }^{\circ}\text{C}$. Fibres were placed within the system (in the sample tube), under vacuum, at least 12 h before the test started, which allowed for extraction of a significant part of the stored moisture within the fibres. A Hiden HPR-20 QIC mass spectrometer (MS) 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 $^{\circ}\text{C}$ to room temperature. First, coir fibre volatiles were separated into four major fractions, while palm fibre volatiles were separated into three (as from the coir run it was seen that three was sufficient). All volatiles were then analysed by FTIR using a PerkinElmer Spectrum 100 in transmission mode.

2.4 Heat treatment of fibres and observation

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

[Type here]

where the initial degradation is observed. Three different temperatures (180, 200 and 220 °C) and two different treatment times (10 and 30 mins) were used.

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 under air 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 min. The temperature was then kept constant for the length of the treatment. Afterwards, the samples were taken out of the oven and cooled down at room temperature. The same procedure was followed to treat coir fibres in a vacuum oven under nitrogen at 220 °C for 30 min.

Fibres for diameter and surface observation, were also individually separated until no fraying could be seen with the naked eye. They were then positioned on a glass slide and fixed with double-sided 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 with a 10x objective lens. The assembly of the fibres mounted on to the glass slide was then 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 the same point as before. Finally, in each picture, the diameter was measured at three different points along the fibre length. The final value for the diameter was taken as the average of these three measurements. The surface of these fibres was then examined, after gold coating, using a HITACHI SU-6600 Field Emission Scanning Electron Microscope.

2.5 Single fibre tensile test

[Type here]

The single fibre tensile testing was designed as a set of experiments that analysed the mechanical properties of date palm and coir fibres before and after heat-treatment. For each different condition, 30 fibres were tested. A gauge length of 20 mm was used for testing non-treated and treated fibres. In the case of non-treated fibres, they were tested as received (no pre-conditioning or treatment). The sample preparation and tensile testing has previously been described in detail [14,15]. The various averages obtained for the mechanical properties of fibres treated under different conditions were compared using a Student's t-Test which determines the probability (p-value) of whether two samples are likely to have come from the same two underlying populations that have the same mean. The test applied was two-tailed (both ends of the distribution) and samples were not paired (unequal sample set sizes). If the p-value obtained was less than 0.05 then we assumed that the two average values were statistically different at the 95% confidence level.

3 Results and discussion

3.1 TGA of natural fibres

TGA was used to investigate the thermal stability and degradation of date palm and coir fibres. The mass losses of both fibres, under nitrogen and air atmospheres, are illustrated in Figure 2 and 3. Degradation curves show that both fibres have a similar thermal weight loss behaviour. As expected, the degradation under an oxidative atmosphere (i.e. air) led to a higher mass loss at high temperatures. TGA along with its DTG, revealed a characteristic degradation under nitrogen, where four main regions could be identified. The degradation in the first region (peak 1 in Figures 2 and 3), for temperatures lower than 150 °C, was mainly attributed to the loss of moisture in the fibres [8,16,17]. The second region, between 150 and 300 °C (characterised by a DTG peak, 2' in Figures 2 and 3), is associated with the degradation of hemicelluloses and pectins [8,17-19]. The third region, between 300 and 400 °C (characterised by a DTG peak, 3' in Figures 2 and 3), was related to the degradation of

cellulose. For higher temperatures, lignin degradation is expected to take place. However, due to the nature of lignin, it is expected that, according to some authors [20], its degradation could take place over a wide temperature range.

In the case of the degradation under air, it was observed that the main degradation DTG peak (peak 3 in Figures 2 and 3) was shifted to a lower temperature. In this case, it can also be noticed that the peaks related to hemicellulose and cellulose are less defined. Furthermore, a large DTG peak appeared (peak 4 in Figures 2 and 3) at temperatures above 400 °C. This was attributed to the oxidative decomposition of the charred residue [17]. DTG peak temperatures are detailed in Table 1. It should be noted that DTG peaks are taken from single measurements and so it is not possible to analyse the statistical significance of any differences.

Peak	DTG Peak temperature (°C)	
	Palm	Coir
2	297	-
2'	286	291
3	324	324
3'	341	346
4	446	451

Table 1: Palm and coir DTG peaks.

Above 150 °C, the majority of the moisture that was present in the fibres would have been eliminated, and so further weight loss is directly related to the degradation of fibre components. The behaviour is very similar for both fibres. Moreover, at temperatures under 220 °C, the thermal degradation profile under air and nitrogen is closely comparable, as seen in Table 2. In general terms, dynamic degradation results agree with similar studies on coir

fibre [18,21,22], and further underline the similarities between the thermal behaviour date palm and coir fibres.

Temperature range (°C)	Palm		Weight loss (%)	
	Nitrogen	Air	Nitrogen	Air
150-180	0.12	0.09	0.09	0.09
150-200	0.29	0.30	0.21	0.20
150-220	0.61	0.83	0.46	0.48

Table 2: Fibre weight loss during the dynamic degradation studies.

In the second set of experiments, the decomposition behaviour of palm and coir fibres in air was analysed under isothermal conditions. An initial temperature ramp ($10\text{ }^{\circ}\text{C min}^{-1}$), was followed by an isothermal region at 180, 200 or 220 °C. The results for palm fibres are shown in Figure 4. The trends in weight loss for the coir fibres were almost identical to those seen in Figure 4 for the palm fibres. Natural fibres can quickly absorb moisture from the atmosphere, which could affect TGA measurements. For this reason, in order to compare the different experiments, the weight loss percentage differences between 15 min (i.e. after moisture loss) and 45 min were analysed. Results are summarised in Table 3. The weight loss is similar for both fibres and increased for increasing temperature. It can be noted from Figure 4 that the weight loss was approximately linearly dependent on time, within the isothermal regions.

Isothermal temperature (°C)	Weight loss for 15-45 min (%)	
	Palm	Coir
180	0.55	0.56
200	1.36	1.11
220	4.27	4.65

Table 3. Fibre weight loss during the isothermal degradation studies.

3.2 TVA analysis of natural fibres

In both cases the thermal degradation of date palm and coir fibres under vacuum produced a significantly higher amount of condensable volatiles compared with the non-condensable products. The TVA plots, showing the evolution of the volatiles versus temperature and time for each fibre, are illustrated in Figure 5. The onset degradation temperatures, the evolution rate peak maxima and the relative amount of condensable and non-condensable volatiles are summarised in Table 4. The relative amounts of volatiles have been calculated through the integration of the pressure versus time curves. The onset degradation temperature was defined as the point at which the system pressure exceeded 7×10^{-5} Torr.

From the results in Figure 5 and Table 4, it can be observed that both fibres have a similar degradation profile, with a main degradation peak at a temperature of approximately 357 °C. The shape of the degradation profile is defined by a main peak (2' in Figure 5), preceded by a large shoulder at a temperature of approximately 300 °C (1' in Figure 5), and followed by a smaller broad shoulder. Furthermore, onset degradation temperatures were almost identical for both fibres, being 197 °C for date palm and 200 °C for coir, indicating that both fibre types have similar thermal stability profiles.

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

Table 4. TVA results summary

Total-volatiles pressure profiles showed good correlation with the DTG curves from the TGA dynamic studies under nitrogen atmosphere in Figures 2 and 3. It should be noted that the initial moisture loss in the TGA curves was not observed in the TVA results due to the fact that fibres were placed in the sample tube under vacuum for 12 h prior to heating. This pre-

[Type here]

conditioning at extremely low pressure, allowed the fibres to release all their moisture. A significant amount of non-condensable volatiles evolved from both fibres, as illustrated in Table 4. The pressure profile of non-condensable volatiles was divided in 4 regions, as illustrated in Figure 5. These regions were analysed by online MS, which indicated that peaks 1 and 2, in the case of both fibres, mainly consisted of carbon monoxide. In regions 3 and 4, with similar results for both fibres, the MS revealed a mixture of carbon monoxide, methane and hydrogen.

The collected condensable volatiles from both fibres in the first stage of the analysis were separated into different fractions by sub-ambient differential distillation and characterised by online MS and gas-phase FTIR analysis. The differential distillation pressure profiles and distillation fractions (i.e. coir C-Fi and date palm P-Fi) for each fibre are represented in Figure 6. The individual peaks (numbered from 1 to 4) represent discrete components of the total volume of collected volatiles. It can be noticed that the pressure profile during differential distillation was almost identical for the two different fibres, and therefore, degradation products were expected to be extremely similar.

It should be pointed out that, due to the TVA line configuration, within the sub-ambient differential distillation process, minor inter-experiment differences may have arisen due to differences in room temperature and manual handling of liquid nitrogen. Differences between both fibres in region 4 of Figure 6, for which the main component was water, could have been caused by the previously mentioned variability. The main component of each peak was identified by online mass spectrometry and FTIR analysis (shown in Figures 7 and 8) as: 1- CO_2 , 2-Formaldehyde and 3-water. Traces of other volatiles were also identified: methanol, ketenes, acetic acid and long aliphatic fragments from unknown long hydrocarbon molecules.

[Type here]

These results agree with the studies on pyrolytic degradation of biomass' main components (i.e. cellulose, hemicellulose and lignin) [6,20,23] and wood species [24]. This thermal degradation analysis represents a general study of the degradation process of palm and coir fibres. Due to the high temperatures achieved during the analysis, a high level of fibre degradation was expected. Consequently, the number of fragments (especially long aliphatic compounds) from low temperature degradation products was high, making it difficult to trace back the initial degradation products.

Both the palm and coir fibres were found to be very brittle after TVA analysis. Figure 9 shows a SEM micrograph of the internal structure of a date palm fibre before and after TVA. It can be seen that major parts of the cell structure have significantly been degraded by the TVA. The structural degradation pattern was in good agreement with the degradation of the three main components of natural fibres: cellulose, hemicellulose and lignin. Each individual cell in these fibres 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 [25]. In the external layers the lignin content is much higher than in the internal layers. Lignin is the most thermally resistant of the main three components [8,26] with a wide degradation temperature range [20]. As observed in Figure 9 the remaining structure of the fibre , after the thermal degradation, was made up of the cell's external walls.

3.3 Fibre observation

It is well known that the accurate measurement of the fibre cross section area is essential to precisely characterise the mechanical properties of natural fibres [27,28]. The comparison of the change in diameter of individual fibres caused by heat treatment at 220 °C for 30 min (as

described in 2.4), is illustrated in Figure 10. From the equations of the least squares fitted straight lines, it can be observed that the measured diameter decreased slightly as a result of heat treatment. The slope of the lines revealed a decrease of approximately 3%. Even though these fibres are not exactly circular in cross section, by assuming that the 3% diameter reduction applies to the fibre width viewed from other angles then this is equivalent to a reduction of about 6% in the fibre cross section area. The reduction provides further evidence of the structural degradation, which was also observed to a greater extent, after high temperature non-oxidative thermal degradation in the TVA (see Figure 9). Figure 11 SEM images from pre and post-heated fibres (at 220 °C for 30 minutes). No significant differences in the surface of the fibres were observed.

3.4 Degradation of mechanical properties

Single fibre tensile testing of non-treated and heat-treated palm and coir fibres revealed fundamental changes in their mechanical properties. The results for average fibre tensile strength, strain to failure and Young's modulus are illustrated in Figures 12-14, where error bars represent 95% confidence limits. In this case the fibre length extension in the “strain” calculation was defined by the crosshead displacement. For both fibres, there was a drop of the tensile strength after heat treatment (see Figure 12). The duration of the treatment also had a clear influence. The 10 min heat treatments reduced the average tensile strength less than the respective 30 min treatments. It can be seen if Figure 12 that, for the case of the 10 min treatments, the tensile strength of date palm is approximately constant for 180 and 200 °C. A two- sample t-test of the average values of non-treated palm in comparison with the 10 min. treatments 180, 200 and 220 °C, only revealed a significant difference at 95% confidence level for the 220 °C treatment (p-value = 0.002). Furthermore, a two- sample t-test of the average values showed no significant difference at 95% confidence level, between

[Type here]

the tensile strength of non-treated palm and when heat treated for 30 min 180 °C (p-value = 0.102).

A different scenario was observed for coir fibre results in Figure 12, where a degradation of tensile strength was observed for all treatments. As might be expected from the TGA isothermal studies under air and nitrogen, the heat treated coir fibres at 220 °C for 30 min. under nitrogen, showed a lower drop of the tensile strength in comparison with the equivalent samples treated on air. In this regard, a two-sample t- test of the average values showed a significant difference at 95% confidence level (p- value = 0.018). However, when comparing 220 °C 30 min. nitrogen and 220 °C 10 min. air, no significant difference was observed at 95% confidence level (p-value = 0.298). It should also be noticed that the values of tensile strength of both fibres, after the 30 min. heat-treatments, are very similar.

In the results of the strain at failure of heat treated fibres in Figure 13, a more severe drop in performance is observed for both fibre types after heat treatment. Similar to the results for tensile strength, the decrease of the strain to failure increased for increasing treatment time and temperature. In the case of treatments at 180 °C, average values were equivalent for 10 and 30 min. For palm, a two-sample t-test of the average values showed no significant difference at 95% confidence level (p-value = 0.074). In the case of coir, values were even more similar, where a two-sample t-test of the average values showed no significant difference at 95% confidence level (p- value = 0.861). As in the analysis of tensile strength, coir fibres heat-treated under nitrogen showed a lower drop of the strain to failure.

In terms of the Young's modulus of heat-treated fibres, no consistent evidence of mechanical performance degradation is observed in the results in Figure 14. In fact, for some of the heat-

[Type here]

treatments, an apparent increase of the average values of Young's modulus can be seen. For palm fibres, two-sample t-tests of the average values revealed no significant difference at 95% confidence level between non-treated and heat-treated samples, with the exception of heat-treated fibres at 200 °C for 10 min. (p -value = 0.007). With regard to coir fibres, two-sample t-tests of the average values revealed no significant difference at 95% confidence level between non-treated and heat-treated samples, with the exception of heat-treated fibres at 220 °C for 10 min and 220 °C for 30 min under nitrogen atmosphere (p -values equal to 0.002 and 0.035, respectively). Although the evaporation of water from the fibres during heat treatment might explain a rise in the fibre modulus, such an explanation would imply that all the heat treated sample would exhibit a rise in modulus. This is clearly not the case in Figure 14. In fact, the variability of the fibre modulus results appears to be related to the very high variability of the cross section area of these natural fibres. In a separate study it has been shown that the measured fibre modulus for these fibres is dependent on fibre dimensions [15] with thicker fibres exhibiting lower average values of modulus.

Figure 15 shows typical examples of the stress-strain curves obtained from the single fibre tensile testing of the coir and palm fibres before and after heat treatment. The curves shown are for individual fibres whose stress-strain curves reflected the average mechanical property values presented in Figures 12-14. In the results for the untreated fibres there is an initial elastic deformation region, up to about 2% strain, above which there is a longer plastic deformation region. Coir and palm are both fibres with high cellulose microfibril angle (MFA) [1,25,29,30]. Such fibres normally exhibit bi-phasic stress-strain behaviour, which is related to the variation of MFA during deformation [29,31] and the interaction between cellulose microfibrils and the rest of the cellular wall matrix components [31]. It has been pointed out that after the yielding point, the matrix materials of the cellular walls (i.e. mainly

[Type here]

hemicellulose, lignin, pectin) undergo plastic deformation while cellulose microfibrils slide with respect to each other [31].

In the case of heat-treated fibres, especially after heat-treatments at 220 °C for 30 min., major changes within the second region of the stress-strain curves were observed. This second region was entirely suppressed in most of the cases after 30 min at 220 °C, as illustrated in Figure 15. Heat-treatment temperatures (i.e. 180, 200 or 220 °C) were expected to mainly degrade pectins and hemicelluloses [17,26], as these components were associated with the initial degradation processes identified by dynamic TGA and TVA experiments. Pectins are one of the main components that cements elementary fibres together. Hemicelluloses are the main component of the secondary wall matrix material, where cellulose microfibrils are embedded, and are meant to bind cellulose and lignin [25]. It is proposed that the degradation of these two components may limit their plastic deformation (i.e. the second region of the fibre stress-strain curve), ultimately leading to sudden failure of the natural fibre. Therefore, degradation of pectins and hemicelluloses would be directly related to the strain to failure and consequently with the tensile strength. On the other hand, at these heat treatment temperatures the cellulose microfibrils which are the main contributor to fibre's rigidity, are not expected to degrade. This is supported by the results from the dynamic TGA and TVA experiments. Cellulose degradation was associated with the second DTG degradation peaks, identified at 324 °C for palm and coir fibres. This is far above the heat-treatment temperatures used here. This may explain the observation in Figure 14 that the average Young's modulus did not decrease after fibre heat treatments.

These results all indicate that thermal treatment, for instance during composite processing, of coir or palm leaf fibres above a temperature of 180 °C will result in a serious reduction of

[Type here]

these fibre's reinforcing ability in composites. This thermally induced loss in fibre reinforcement performance does not appear to be limited to the two fibres used in this study. Yao *et al* [32] studied the thermal decomposition kinetics of ten different natural fibres including wood, bamboo and bast fibres. Even under a nitrogen atmosphere an onset decomposition temperature range of about 215 ± 10 °C was measured for all natural s except for pine fibre with approximately 60% of the thermal decomposition occurring in a temperature range between 215 °C and 310 °C which they noted overlaps with the processing temperatures of many thermoplastics. Gassan and Bledzki studied the effect of heat treatment on the performance of both flax and jute yarns [4]. For temperatures above 170 °C the tenacity decreased rapidly. Higher temperatures and longer exposure times to a drop in tenacity. Treatment at a temperature of 210 °C resulted in a drop in tenacity of approximately 70%. In a study of the effects of heat treatment on the mechanical properties of flax bundles Van Velde [10] concluded that composite production temperatures higher than 180 °C have to be avoided to minimise loss of reinforcement performance of the flax fibres. Teixeira *et al* performed tensile testing on curaua, hemp and sisal fibres which had been treated at temperatures up to 200 °C [33]. They found that all fibres exposed at 200 °C became fragile and brittle and exhibited drastic decreases (>90%) in tensile strength and strain to failure. Finally, a recent wide ranging review of the thermal stability of natural fibres and their polymer composites by Asim *et al* and confirmed that the thermal degradation of natural fibres above processing temperatures of 200 °C is an issue [3]. Consequently it appears highly advisable that processing temperatures for natural fibre reinforced composites should be kept as low as possible and certainly below 200 °C.

4 Conclusions

[Type here]

This work has shown the importance of controlling the processing conditions of coir and date palm fibres in composite production due to the possibility of thermal degradation. It is clear from the results presented here that, when producing composite materials with these fibres, processing temperatures should be minimised as much as possible and certainly kept below 200 °C.

Dynamic thermal analysis of both fibres under nitrogen revealed two characteristic peaks from the derivative of thermogravimetric analysis (DTG) that were associated with pectin-hemicellulose and cellulose degradation. Lignin degradation peaks were not clearly observed. Under air atmosphere, DTG peaks were slightly shifted to lower temperatures. At the same time, an additional peak at high temperatures, attributed to the oxidative decomposition of charred residue, was detected. Isothermal TGA studies showed higher weight loss for higher temperatures and longer exposure times. Equivalent experiments under nitrogen, showed lower weight loss in comparison with experiments under air. The thermal behaviour of palm and coir was also explored using the TVA technique, under vacuum. Long exposure (12 hours) to vacuum at room temperature proved to be effective to remove the moisture absorbed by the fibres. Similar degradation patterns, in comparison with TGA under nitrogen, were observed in the TVA pressure profile. MS and FTIR were used to investigate the considerable amount of volatiles from the degradation processes. The main components identified were carbon monoxide, methane, hydrogen, carbon dioxide, formaldehyde and water. Traces of other volatiles were also identified: methanol, ketenes, acetic acid and long aliphatic fragments from unknown long hydrocarbon molecules. Further investigation of the fibres analysed in the TVA, under the SEM, revealed high structural degradation of the external cells and the secondary layer of internal cells.

[Type here]

The analysis of palm and coir fibres, before and after heat-treatment (at 220 °C for 30 min.), revealed a decrease of their cross sectional area of approximately 6%. At the same time, no significant fibre surface morphology changes were observed using SEM. Single fibre testing of palm and coir fibres heat-treated under air atmosphere showed a significant drop in the failure strain and tensile strength, especially at processing temperatures above 200 °C. Furthermore, above 200 °C, a clear time dependence of the degradation was also observed. However, the average fibre Young's modulus values remained almost constant with heat treatment. Coir fibres heat-treated at 220 °C for 30 min. under nitrogen atmosphere showed a lower drop in tensile strength and failure strain than the equivalent air treatment. In the case of both fibres, these heat treatments at 180-220 °C were mainly associated with the degradation of pectins and hemicelluloses, which only affected the high strain region of the stress-strains curves. Consequently, this led to a significant drop of the natural fibre tensile strength and failure strain, especially after high temperatures and long exposures. The initial low strain elastic region, where the Young's modulus is measured, remained relatively unaffected. The direct observation of fibres and the analysis of the tensile data showed that the thermal degradation affects the structural integrity and mechanical properties of these natural fibres.

Acknowledgements

The authors gratefully acknowledge the financial support of SABIC Petrochemicals B.V. and the EPSRC Doctoral Training Grant scheme.

References

1. Peças P, Carvalho H, Salman H, Leite M. Natural fibre composites and their applications: A review. J Compos Sci 2018;2:66.

2. Sahu P, Gupta M. A review on the properties of natural fibres and its bio-composites.
Proc IMechE Part L: J Materials: Design and Applications 2020;234:198-217.
3. Asim M, Paridah MT, Chandrasekar M, Shahroze RM, Jawaid M, Nasir M, Siakeng R.
Thermal stability of natural fibers and their polymer composites. Iran Polym J 2020;29:625–648.
4. Gassan J, Bledzki AK. Thermal degradation of flax and jute fibers. J Appl Polym Sci 2001;82:1417–1422.
5. Stamm AJ. Thermal degradation of wood and cellulose. Ind. Eng. Chem. 1956;48,413–417.
6. Schwenker RF, Pacsu E. Pyrolytic degradation products of cellulose. Ind Eng Chem Chem Eng Data Series 1957;2:83–88.
7. Roberts AF. A review of kinetics data for the pyrolysis of wood and related substances. Combust Flame 1970;14:261–272.
8. Tajvidi M, Takemura A. Thermal degradation of natural fiber-reinforced polypropylene composites. J Thermoplast Compos Mater 2009;23:281–298.
9. Nuñez AJ, Kenny JM, Reboreda MM, Aranguren MI, Marcovich NE. Thermal and dynamic mechanical characterization of polypropylene-woodflour composites. Polym Eng Sci 2002;42:733–742.
10. Van de Velde K, Baetens E. Thermal and mechanical properties of flax fibres as potential composite reinforcement. Macromol Mater Eng 2001;286:342–349.
11. Thomason JL, Rudeiros-Fernández JL. Evaluation of injection moulded natural fibre-polyolefin for potential in automotive applications. Front Mater 2018;5:60.
12. Thomason JL. The influence of fibre length and concentration on the properties of glass fibre reinforced polypropylene: 5) Injection moulded long and short fibre PP. Compos Pt A Appl Sci Manuf 2002;33:1641-1652.

13. McNeill IC, Ackerman L, Gupta SN, Zulfiqar M, Zulfiqar S. Analysis of degradation products by thermal volatilization analysis at subambient temperatures. *J Polym Sci Polym Chem Ed* 1977;15:2381–2392.
14. Fernández JLR, Thomason JL. Characterisation of the mechanical performance of natural fibres for lightweight automotive applications'. Paper 1231, Proceedings of 15th European Conference on Composite Materials, Venice, Italy, June 2012.
15. Thomason JL, Rudeiros-Fernández JL. Modelling the influence of fibre internal structure on the measured modulus of natural fibres. *Compos Pt A Appl Sci Manuf* submitted 2021.
16. Bismarck A, Aranberri-Askargorta I, Springer J, Mohanty AK, Misra M, Hinrichsen G, Czapla S. Surface characterization of natural fibers; surface properties and the water uptake behavior of modified sisal and coir fibers. *Green Chem* 2001;3:100–107.
17. Rachini A, Le Troedec M, Peyratout C, Smith A. Comparison of the thermal degradation of natural, alkali-treated and silane-treated hemp fibers under air and inert atmosphere. *J Appl Polym Sci* 2009;112:226–234.
18. Varma DS, Varma M, Varma IK. Thermal behaviour of coir fibres. *Thermochim Acta* 1986;108:199–210.
19. Raveendran K, Ganesh A, Khilar KC. Pyrolysis characteristics of biomass and biomass components. *Fuel* 1996;75:987–998.
20. Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 2007;86:1781–1788.
21. Silva GG, Souza DADE, Machado JC, Hourston DJ. Mechanical and thermal characterization of native brazilian coir fiber. *J Appl Polym Sci* 2000;76:1197–1206.

22. Tomczak F, Sydenstricker THD, Satyanarayana KG.: Studies on lignocellulosic fibers of Brazil. Part II: Morphology and properties of Brazilian coconut fibers. *Compos Pt A Appl Sci Manuf* 2007;38:1710–1721.
23. Lipska AE, Wodley FA. Isothermal pyrolysis of cellulose : Kinetics and gas chromatographic mass spectrometric analysis of the degradation products. *J Appl Polym Sci* 1969;13:851-865.
24. Müller-Hagedorn M, Bockhorn H, Krebs L, Müller U. A comparative kinetic study on the pyrolysis of three different wood species. *J Anal Appl Pyrolysis* 2003;68:231–249.
25. Mussig J, editor. Industrial applications of natural fibres: structure, properties, and technical applications. Chichester: John Wiley & Sons, 2010.
26. Herrera A, Soria S, Araya CP. A kinetic study on the thermal decomposition of six hardwood species. *Holz als Roh- und Werkst.* 1986;44:357–360.
27. Thomason JL, Carruthers J, Kelly, J, Johnson G. Fibre cross-section determination and variability in sisal and flax and its effects on fibre performance characterisation. *Compos Sci Technol* 2011;71:1008–1015.
28. Thomason JL, Carruthers J. Natural fibre cross sectional area, its variability and effects on the determination of fibre properties. *J Biobased Mater Bioenergy* 2012;6:1–7.
29. Martinschitz KJ, Boesecke P, Garvey CJ, Gindl W, Keckes J. Changes in microfibril angle in cyclically deformed dry coir fibers studied by in-situ synchrotron X-ray diffraction. *J Mater Sci* 2008;43:350–356.
30. Kulkarni AG, Satyanarayana KG, Sukumaran K, Rohatgi PK. Mechanical behaviour of coir fibres under tensile load. *J Mater Sci* 1981;16:905–914.
31. Spatz H, Köhler L, Niklas KJ. Mechanical behaviour of plant tissues: composite materials or structures? *J Exp Biol* 1999;202:3269–3272.

[Type here]

32. Teixeira FP, Gomes OFM, Silva FA. Degradation mechanisms of curaua, hemp, and sisal fibers exposed to elevated temperatures. BioResources 2019;14:1494-1511.
33. Yao F, Wu Q, Lei Y, Guo W, Xu Y. Thermal decomposition kinetics of natural fibers: Activation energy with dynamic thermogravimetric analysis. Polym Degrad Stab 2008;93:90-98.

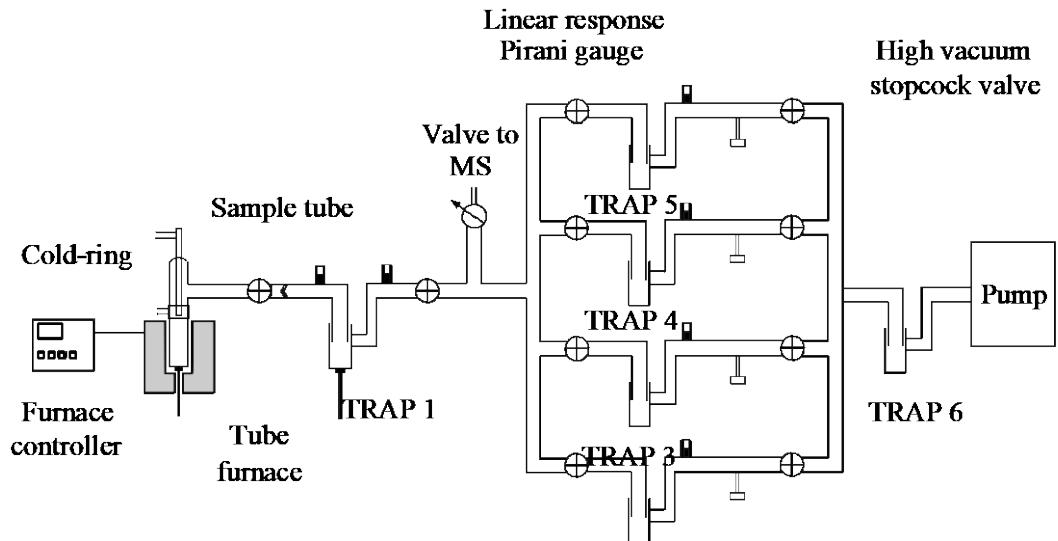


Figure 1. TVA line diagram.

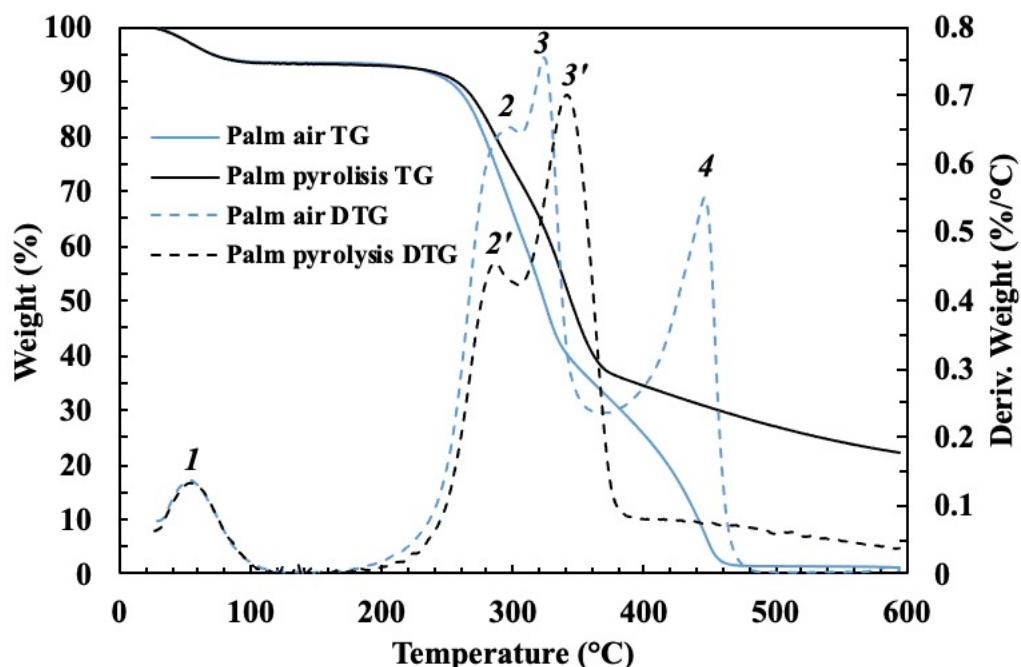


Figure 2. Thermo-gravimetric degradation of palm, under nitrogen and air atmospheres, at the heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

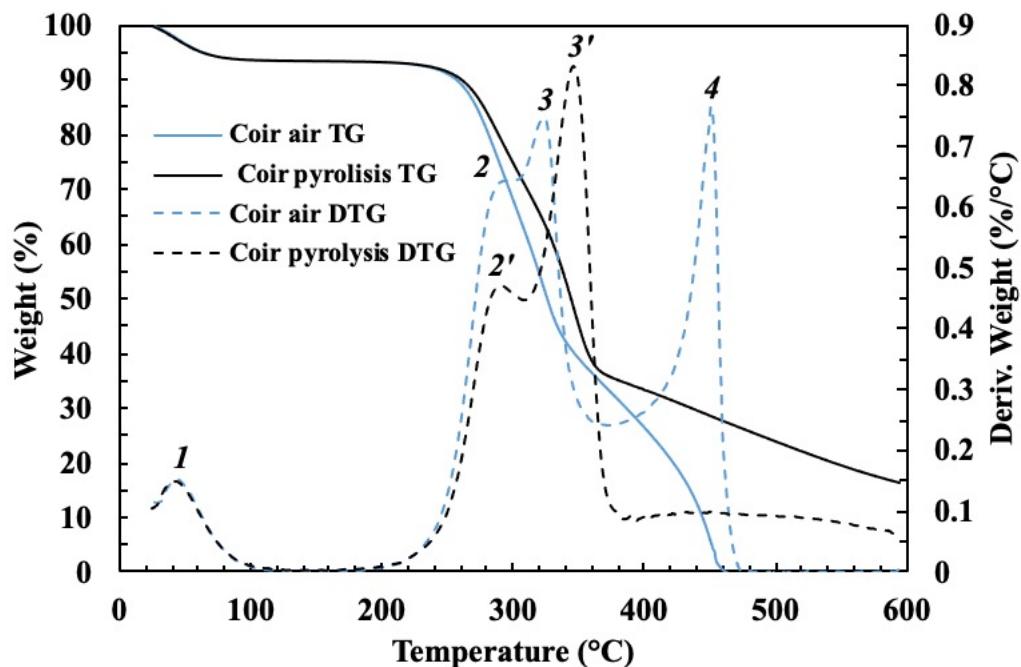


Figure 3. Thermo-gravimetric degradation of coir, under nitrogen and air atmospheres, at the heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

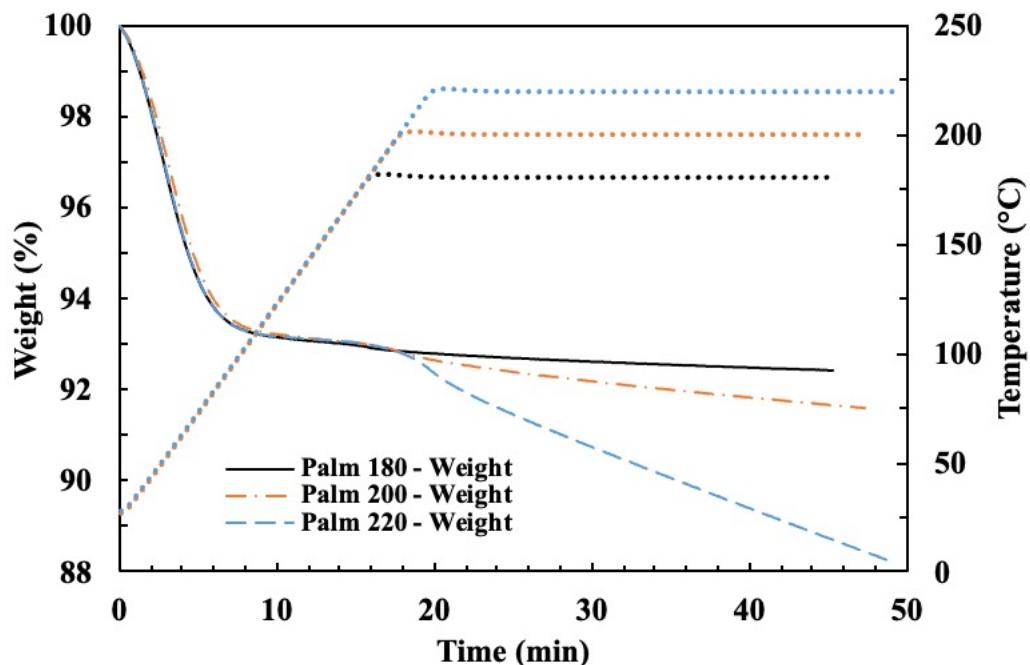


Figure 4. Isothermal degradation of palm, under air atmosphere, at 180 , 200 and 220 $^{\circ}\text{C}$.

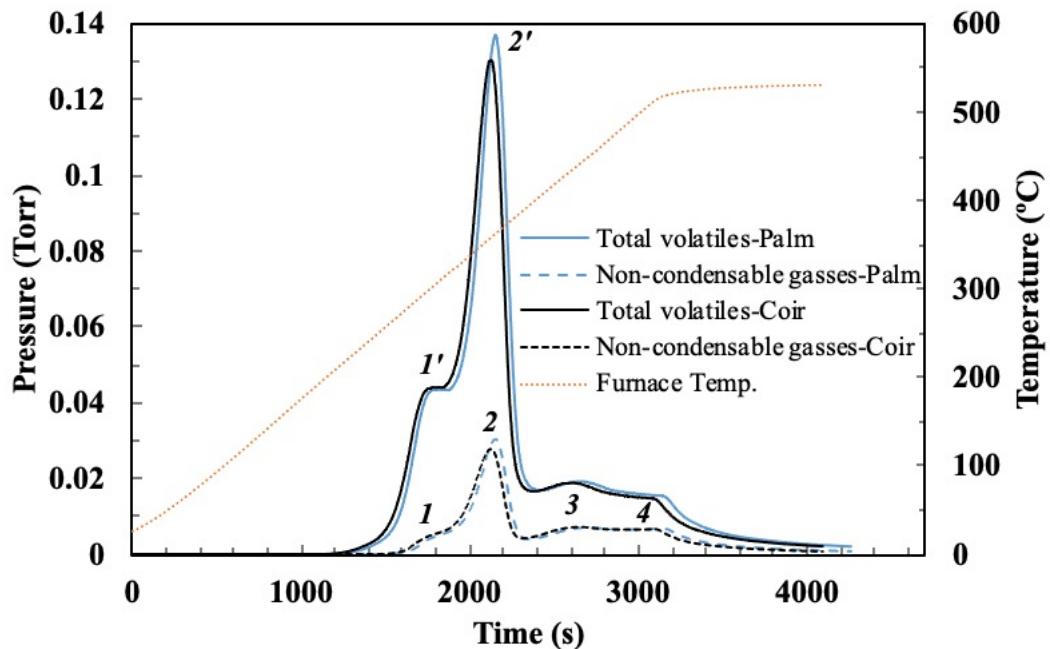


Figure 5. TVA degradation profiles of coir and palm fibres.

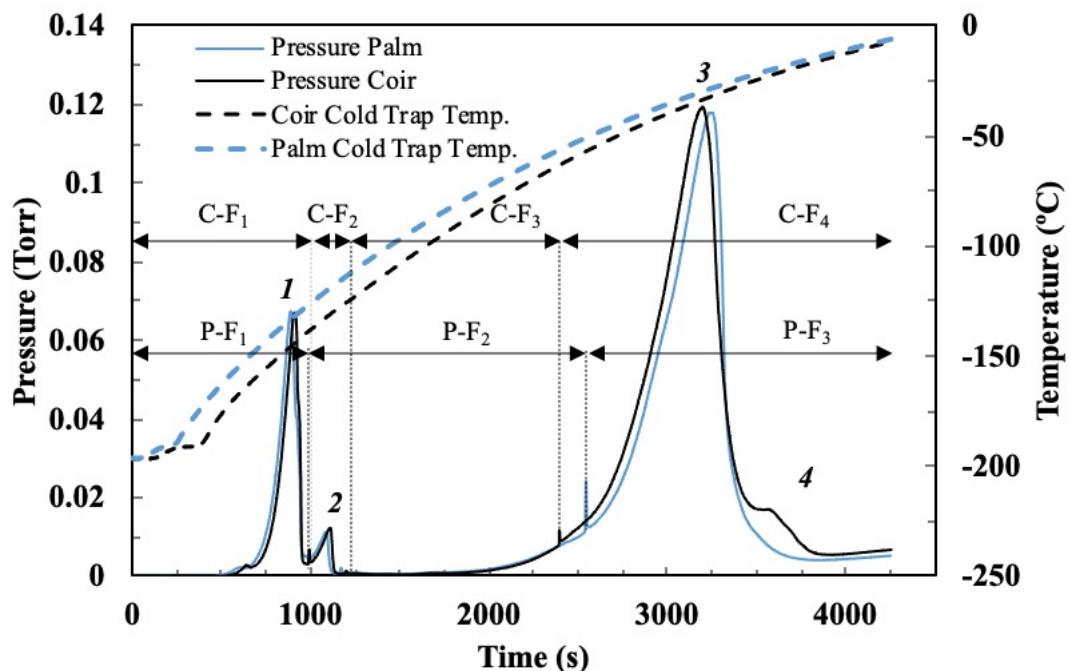


Figure 6. Sub-ambient differential distillation traces for condensable fractions collected from palm and coir.

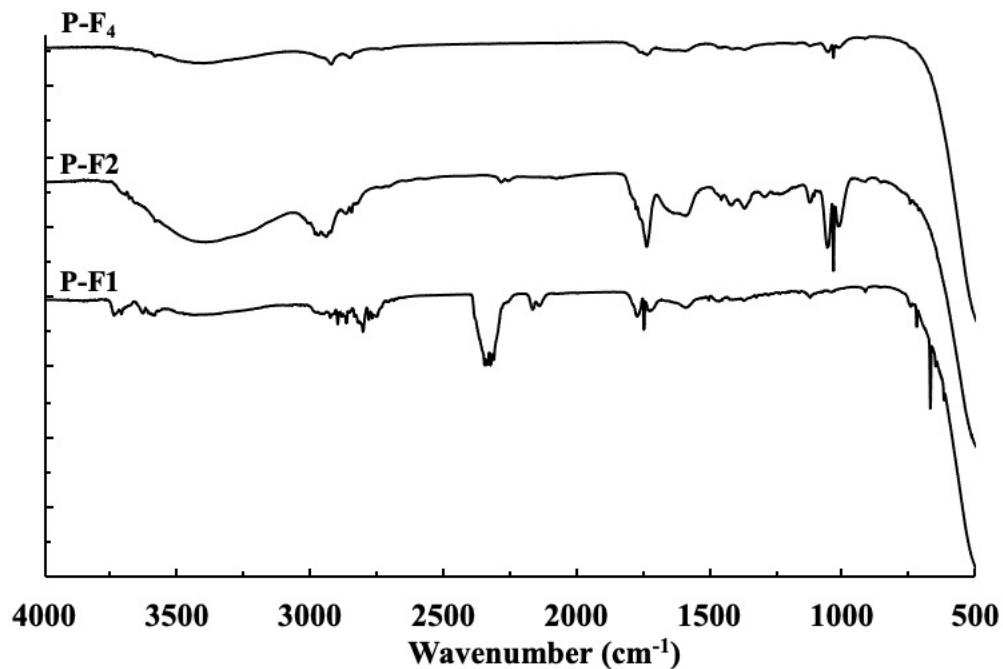


Figure 7. Palm's Transmittance FTIR spectrum of the recovered condensable fractions separated by sub-ambient differential distillation.

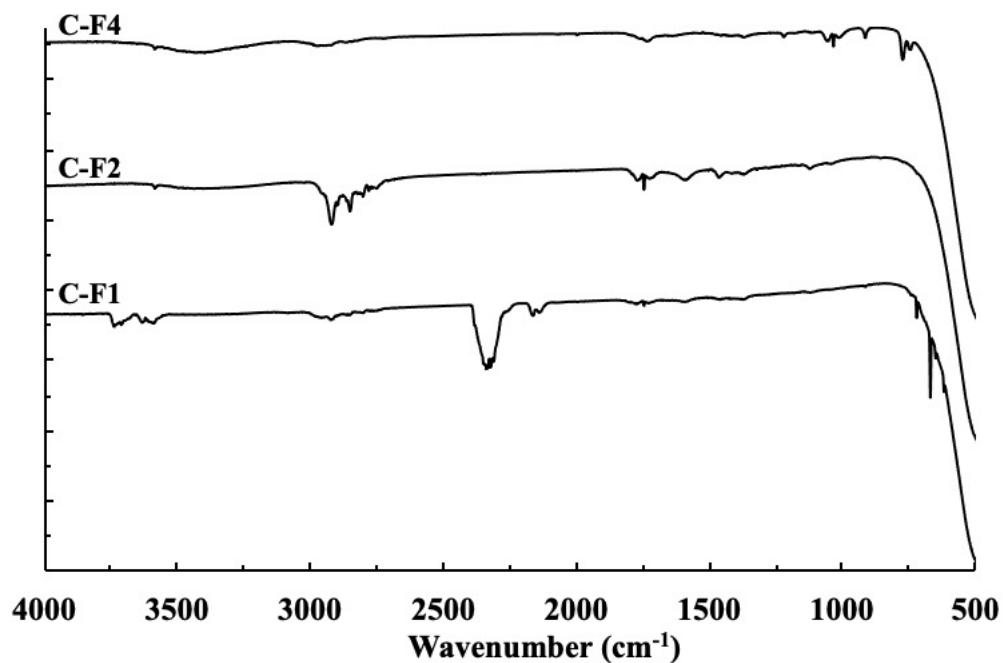


Figure 8. Coir's Transmittance FTIR spectrum of the recovered condensable fractions separated by sub-ambient differential distillation.

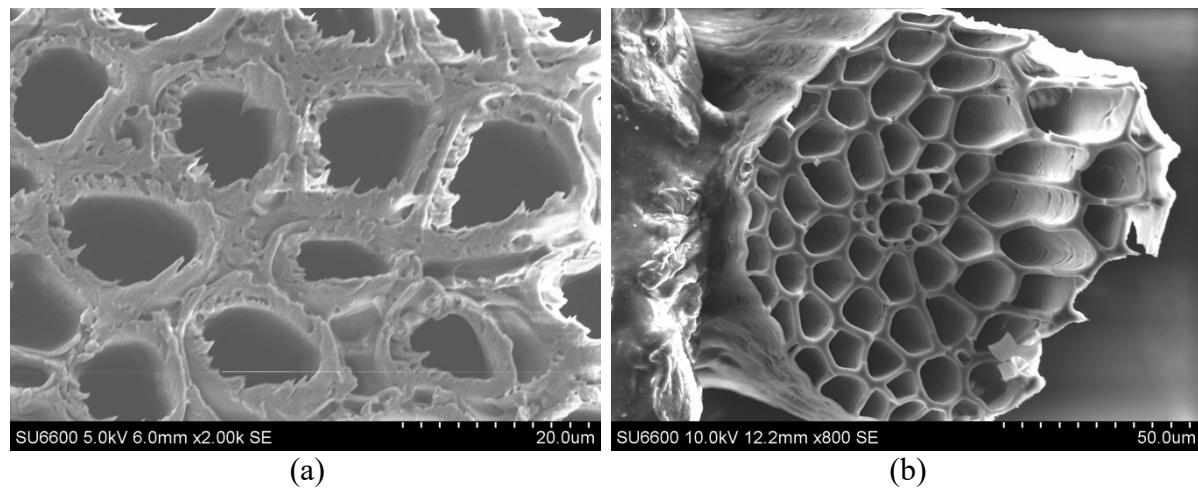


Figure 9. SEM of palm fibre cross sections (a) before and (b) after TVA analysis.

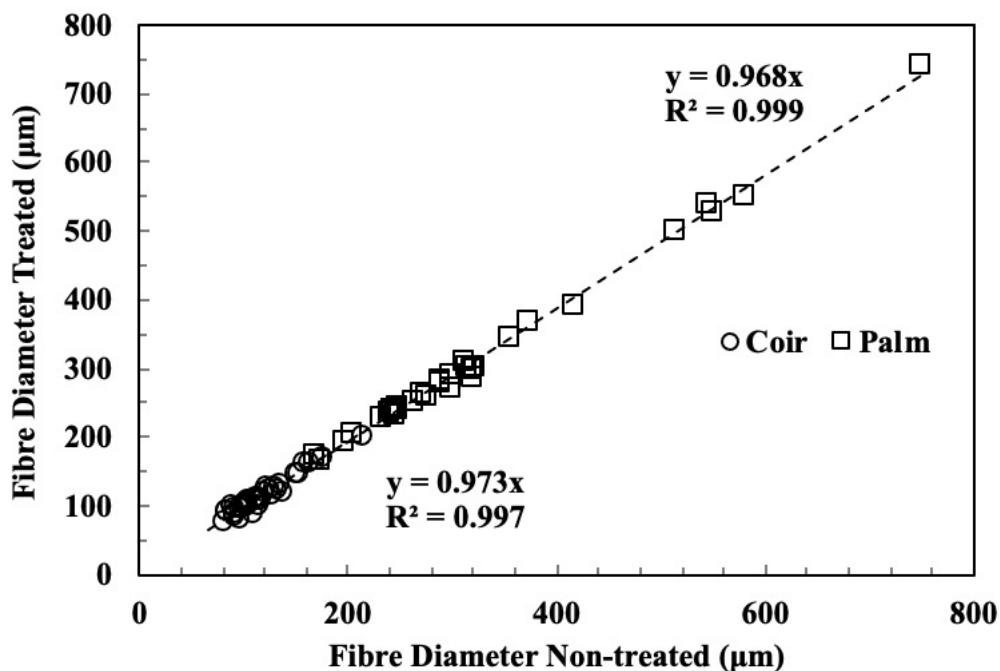


Figure 10. Heat treated fibre diameter versus untreated fibre diameter.

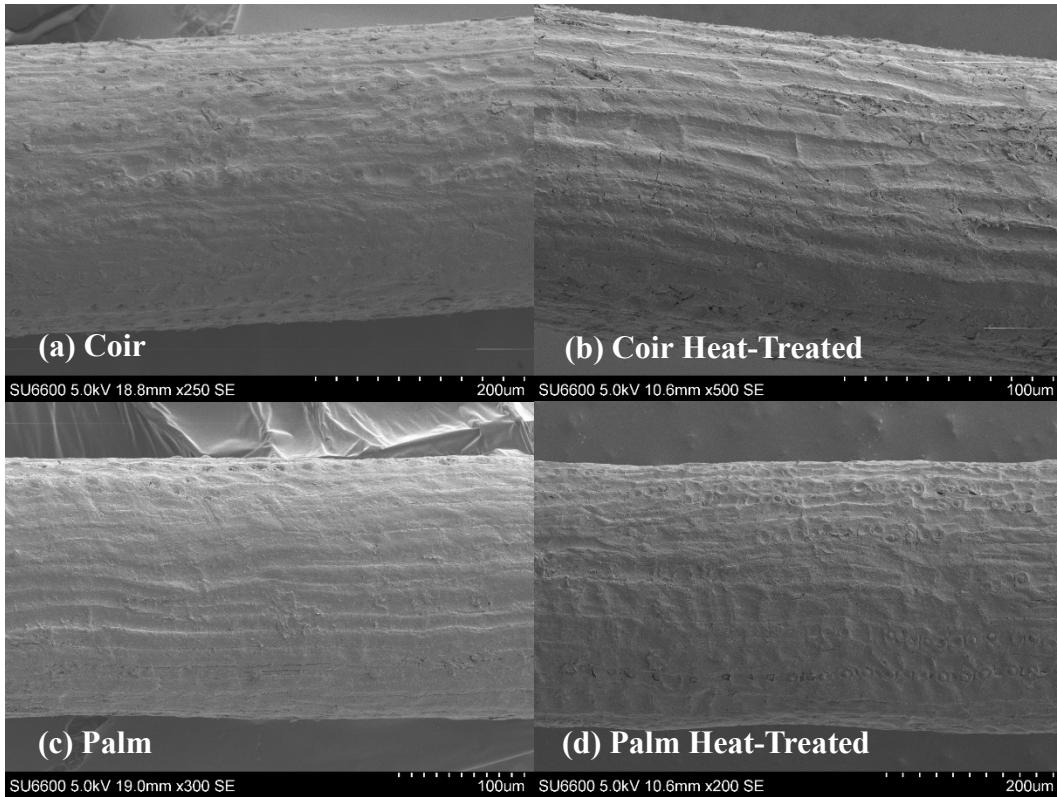


Figure 11. SEM surface observation of treated and non-treated fibres.

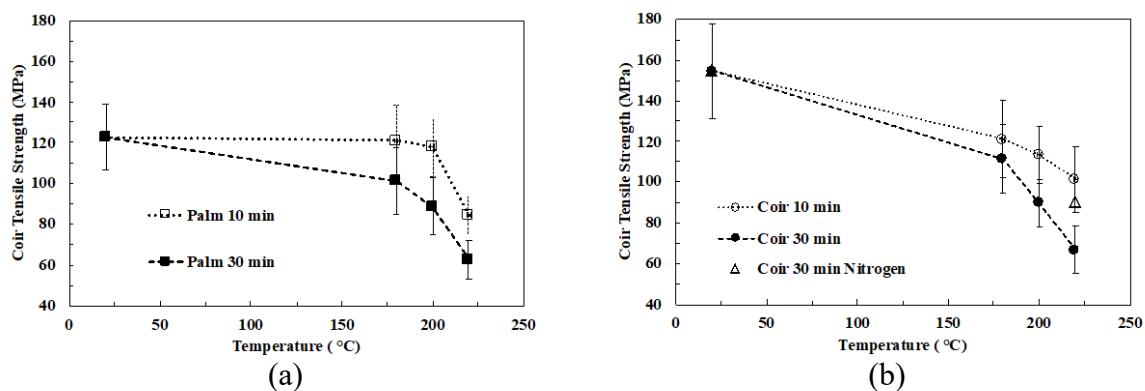


Figure 12. Fibre tensile strength versus heat-treatment temperature. (a) Palm (b) Coir.

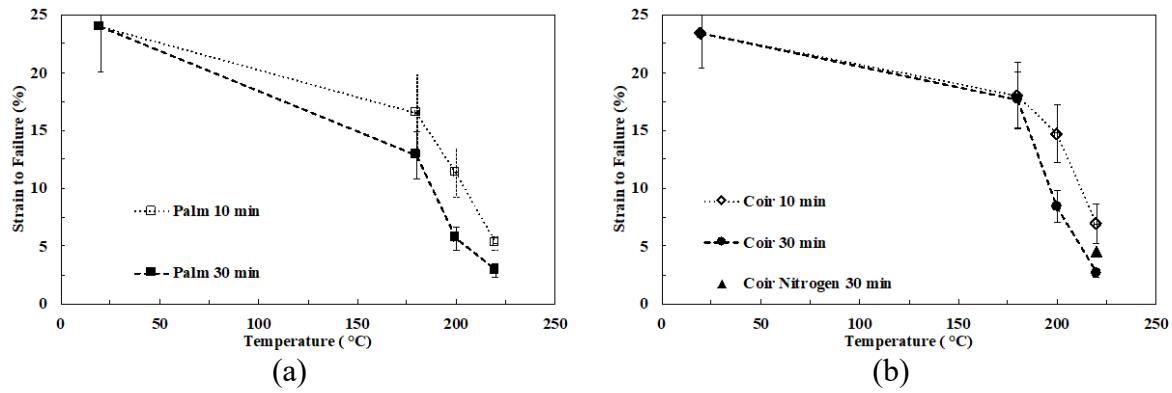


Figure 13. Fibre strain to failure versus heat-treatment temperature. (a) Palm (b) Coir.

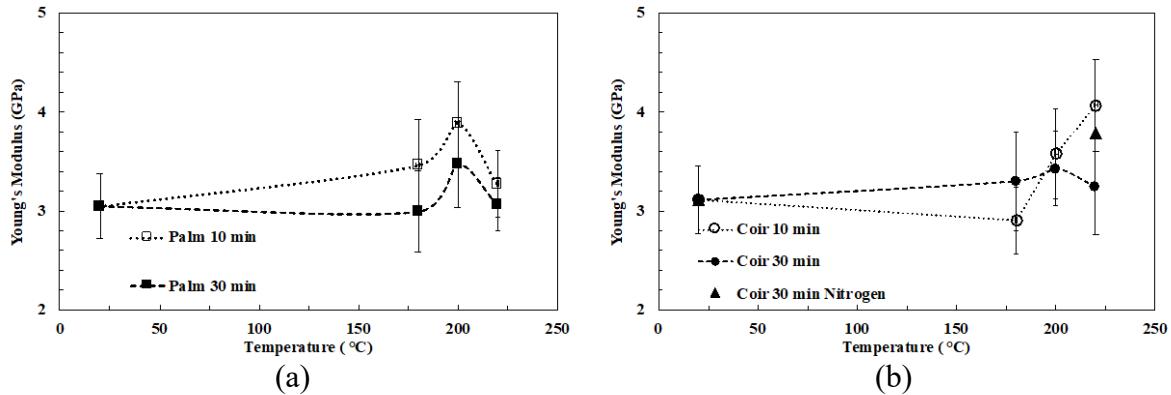


Figure 14. Fibre Young's modulus versus heat-treatment temperature. (a) Palm (b) Coir.

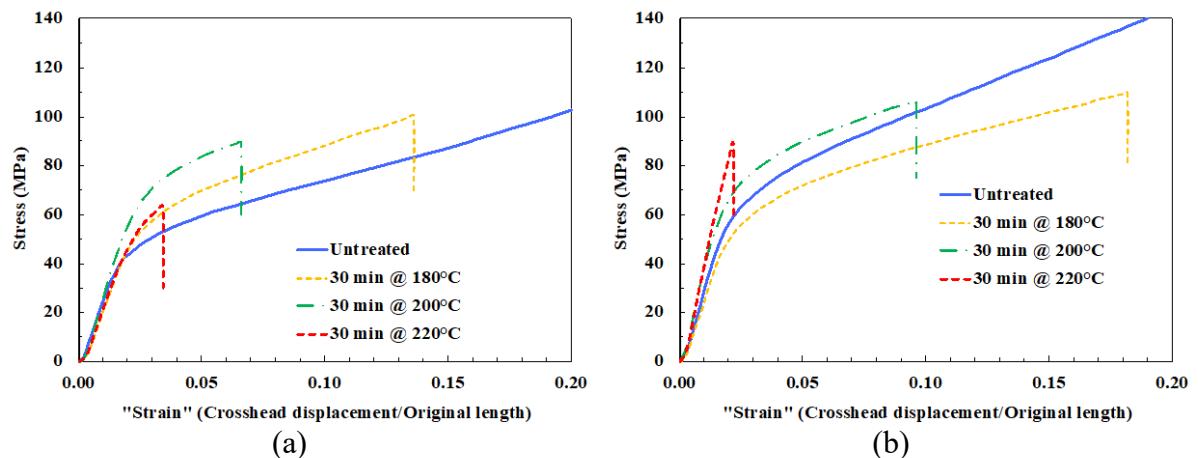


Figure 15. Typical stress-strain curves for fibres heat-treated in air. (a) Palm (b) Coir.