

Preparation and properties of polypropylene composites reinforced with wheat and flax straw fibres

Part I *Fibre characterization*

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The microstructure, thermal and mechanical properties of flax and wheat straw fibres have been examined with a view to using these natural fibres as reinforcing additives for thermoplastics. In this regard, the fibres were characterized prior to incorporation into the polymer, using a range of techniques, including SEM, image analysis, thermogravimetric analysis and micro-mechanical tensile testing, at room and elevated temperatures. The thermal and mechanical properties obtained have been discussed in relation to the measured composition and structural form of the fibres.

1. Introduction

For many years, additives of organic origin have been combined with polymers in order to modify their properties. For example, the presence of starch in thermoplastics can impart biodegradable characteristics to the material, finding widespread application for this purpose [1]. Wood flour has long been used as an additive to thermosetting phenolic resin compositions to enhance impact performance and reduce shrinkage on cure [2]. When contained in thermoplastics, it functions more as a matrix diluent creating a wood-like effect to the material, but frequently with an adverse effect on toughness, depending on the extent of interfacial bonding between filler and matrix [3]. There are also many reports on the use of naturally occurring fibres, including jute, sisal, etc., as reinforcing fibres for polymers [4–6].

Significant improvements in mechanical properties have been achieved with the reinforcing efficiency of fibres further enhanced by chemical modification to promote bonding at the fibre–matrix interface [6]. In this regard, the use of fibres from arable waste sources offer significant potential as low-cost reinforcements for polymers. Some limited work has already been reported with such materials in combination with various polymer matrices [7–9].

In this paper, and in Part II [10], the use of natural fibres derived from comminuted wheat and flax straw waste as functional additives for polypropylene is discussed. Factors influencing their effectiveness as reinforcements are highlighted, with emphasis on the influence of shear and thermal conditions experienced during melt compounding on the structure and properties of the fibres and also the effects of interfacial bonding between the fibres and matrix. Part I considers the microstructure, mechanical and thermal

properties of these fibrous additives, prior to incorporation into the polymer.

2. Experimental procedure

2.1. Materials

Flax fibres were supplied by the Silsoe Research Institute, UK, after retting and decortication procedures, in lengths of approximately 30–40 cm. To facilitate handling, treatment and subsequent compounding with polymer, the fibres were first pulped by passing through a co-rotating twin-screw extruder.

Wheat straw fibres were obtained in hammer-milled form from Compak Systems Ltd UK, and were sieved to remove very coarse fibres, as well as particulate components, to give a mean length of about 2.5 cm.

2.2. Measurement of fibre strength

The tensile strength and elastic modulus of flax and wheat straw fibres were measured using a Rheometrics RSA mechanical analyser, using a static strain sweep programme. This procedure involved gluing individual fibres to a paper frame with an epoxy adhesive and attaching this to thin film grips on the RSA analyser. Before testing, the edges of the supporting paper were cut so that no load was carried by the frame. Specimens were stressed instantaneously to cause failure before reaching a strain limit of 3%, with data points recorded at each 0.1% strain increment.

The cross-sectional area of single flax fibres was assessed using a calibrated graticule eyepiece on a reflectance light microscope, taking an average of five measurements. For the purpose of these experiments, it was assumed that the fibres were perfectly round and of uniform structure throughout their thickness. In the case of wheat straw samples, sections were cut

from the walls of the tubular stem by slicing in the longitudinal direction and their width and thickness measured using a Vernier screw gauge.

In order to establish the extent of possible specimen size effects on fibre properties, samples were examined at 10, 15 and 20 mm gauge lengths. Fibres were also tested at 25, 100 and 200 °C within the temperature-conditioning unit, surrounding the specimens. Samples were exposed to these temperatures for up to 4 min to allow thermal equilibration before determination of their properties.

Prior to testing, fibres were conditioned at 10%–15% relative humidity (at 23 °C) according to BS 3411 (1971).

2.3. Thermal properties of fibres

The thermal stability of flax and wheat straw fibres was determined using a Perkin–Elmer TGS-2 thermogravimetric analyser.

Tests were undertaken in both nitrogen and air atmospheres between 30 and 730 °C, at a heating rate of 5 °C min⁻¹. The arithmetic mean from three determinations was used to obtain values for moisture level, inorganics content and onset of fibre decomposition. Samples of pure lignin (Aldrich Chemical Co. Inc.) and α -cellulose (Svenska Traemjoels–Fabrikerna AB) were also analysed for comparison.

Some measurements on the flax and wheat straw fibres were also carried out under isothermal conditions in an air environment at 190, 210, 230 and 250 °C, by heating for 30 min at each temperature.

2.4. Fibre microstructure and chemical composition

Scanning electron microscopy (SEM) was used to examine the microstructure of the natural fibres before combination with polymer. These were sprinkled on to double-sided adhesive tape attached to aluminium stubs, then coated with gold. Energy dispersive X-ray analysis was also employed to obtain information about the chemical composition of the fibres.

3. Results and discussion

A principle aim of this work was to analyse the structure and properties of wheat and flax straw fibres with a view to assessing their potential as reinforcing additives for polypropylene. Hence emphasis has been given towards characterizing these fibres prior to compounding with the polymer in order to establish a basis for examining changes induced by subsequent melt mixing and injection-moulding processes.

A schematic diagram of the cross-section of wheat straw fibres is shown in Fig. 1. The fibrous form of this material used in this work is itself a composite material, comprising cellulose microfibrils bound within an amorphous matrix of lignin and hemicellulose. Macroscopically, a straw stem comprises internodes separated by nodes, which are the hard points at which the leaves are attached to the stem.

The internodes are formed as concentric rings leaving a void or lumen in the centre. As seen in Fig. 1, the outermost ring is a cellulose-rich dense layer (termed the epidermis) which has a concentration of silica on the surface. Beneath this is a layer of lignin containing 25%–27% by volume of sclerenchyma, or vascular bundles.

Fig. 2 shows the epidermal and inner sclerenchyma structures of wheat straw sections taken from the wall of the stem. The cellular form of the sclerenchyma and parenchyma is clearly evident in Fig. 2b, and in Fig. 2c the epidermis is observed. The small holes on the surface are stomata through which the plant cells can breathe.

The structure of linseed flax is very similar to wheat straw but in addition has a pericyclic ring situated just beneath the epidermis layer containing around 30 bundles of macro-fibres, which are the commercially important extract used in the textile industry [11]. These fibre cells typically have a width between 25 and 125 μ m and a length of 8–30 mm. These are joined together in the form of a chain of fibre cells from the bottom of the stem to the seed-bearing top of the plant, resulting in bundle lengths of between 300 and 900 mm. The form of linseed flax fibres used in this investigation is shown in Fig. 3. Some single-fibre cells are apparent as well as several joined in bundles. The

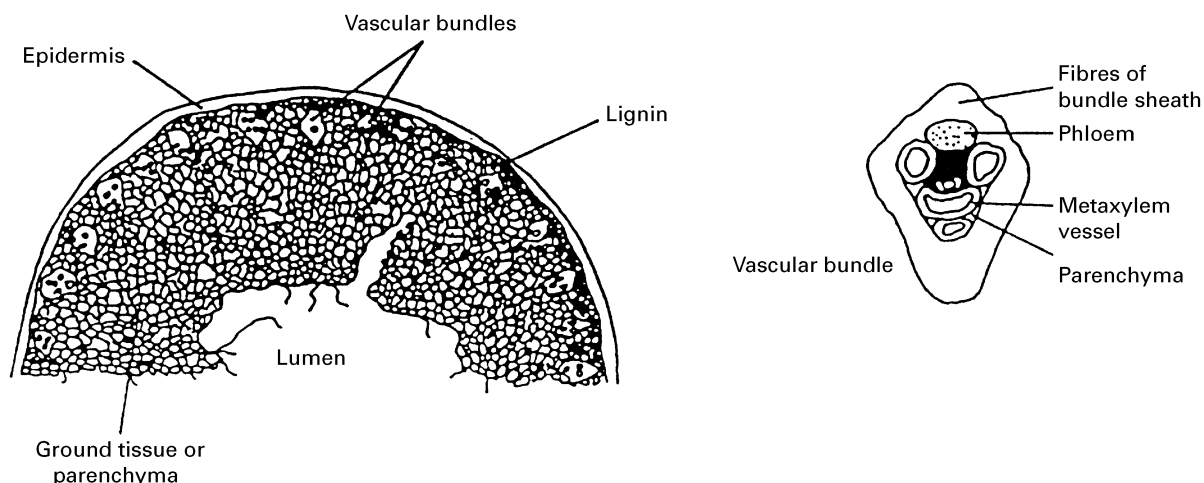


Figure 1 Schematic diagram of the structure of wheat straw (after [7]).

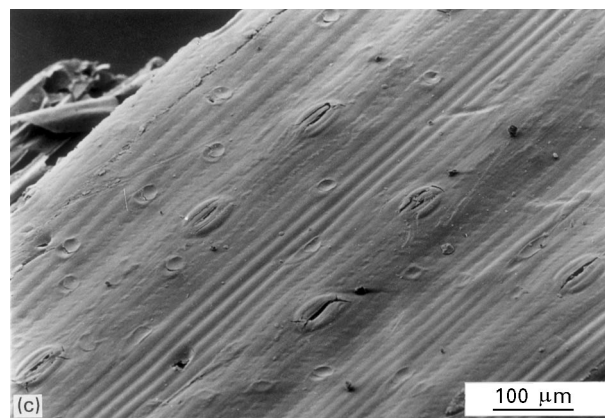
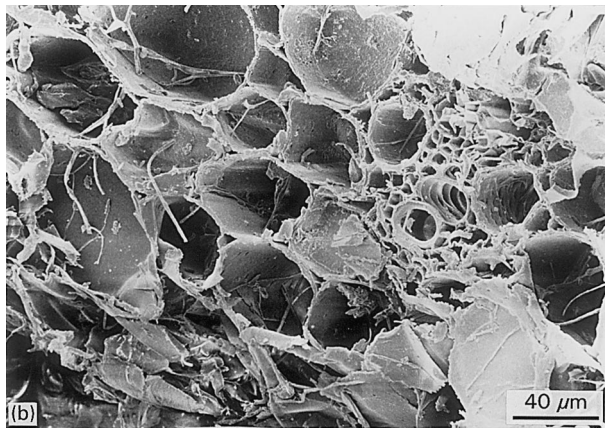
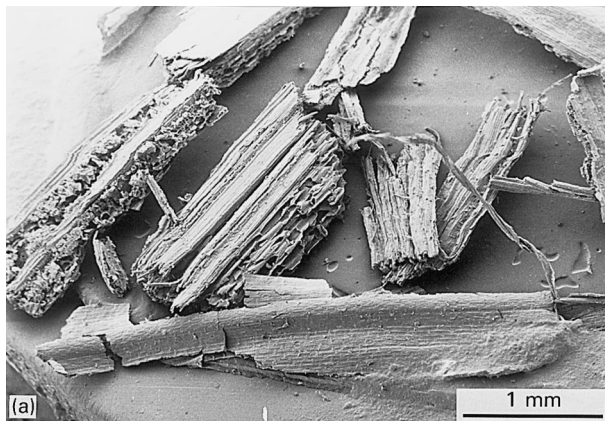


Figure 2 Microstructure of wheat straw: (a) general view of fibres, (b) cellular structure of central region, (c) epidermis of fibres.

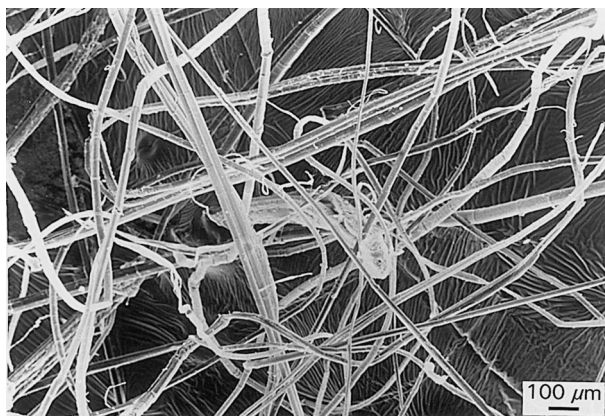


Figure 3 Linseed flax fibres, as-received.

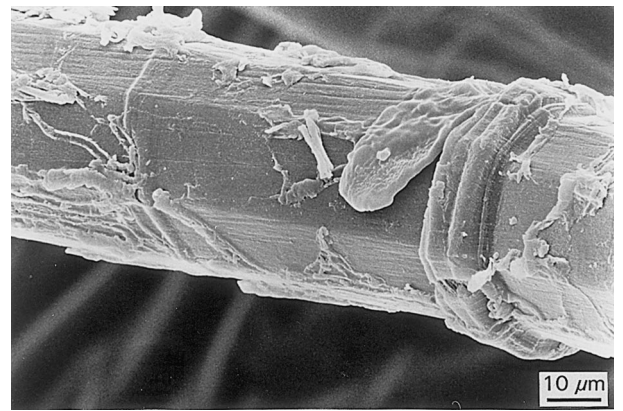


Figure 4 Cross-sectional geometry and structural defects in flax fibres.

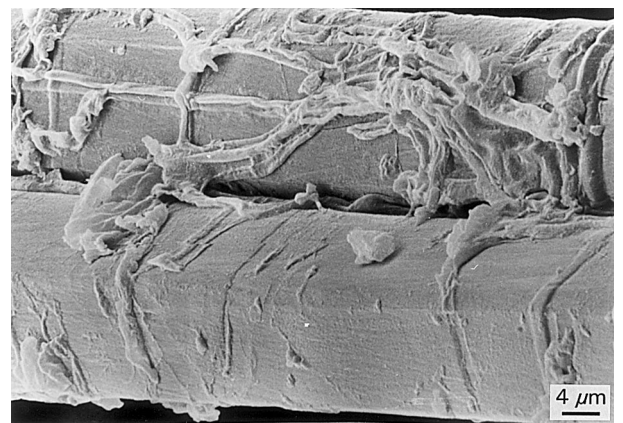


Figure 5 Intercellular binding of flax fibres.

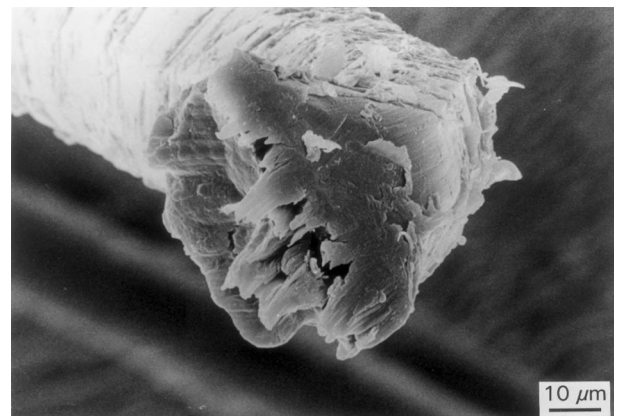


Figure 6 End view of linseed flax fibre.

fibres have a polygonal cross-sectional geometry (Fig. 4), but can contain several hundred dislocations along their length, running transversely across the fibres. These so-called internodes may occur when the fibre cells unite [12], but could also result from mechanical damage to the fibre walls. Intercellular material cementing together individual fibres (Fig. 5) consists of lignin hemicellulose and pectin. Fig. 6 shows the end of a single flax-fibre cell demonstrating the relatively dense nature of this material.

Linseed flax fibres were also subjected to a pulping treatment prior to introducing them into the polymer.

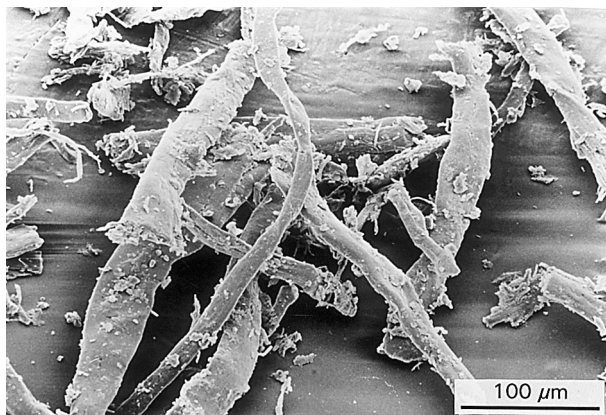


Figure 7 Flax fibres and associated debris after pulping through a twin-screw extruder.

This involved passing the fibres through a co-rotating intermeshing twin-screw extruder in the dry state, and causing the formation of shorter fibres, generally being more ribbon-like in shape (Fig. 7). Considerable amounts of debris also resulted from this process.

Table I gives an indication of principal elements, other than carbon and hydrogen present in the two fibre types under study, as determined by microprobe analysis. It is apparent that the wheat straw contains considerably more silicon (in the form of silica) than the flax, which is located mainly in the epidermis. Furthermore, the flax straw contained more calcium, but less sulfur and potassium than the wheat straw.

In the context of the present investigation, the thermal properties of the natural fibres are of particular relevance, because processing of these materials in combination with polypropylene requires exposure to temperatures approaching 200 °C during both compounding and injection-moulding operations.

Fig. 8 shows isothermal weight-loss curves for flax and wheat straw fibres obtained in air at increasing temperatures. Weight-loss results are compared in Fig. 9 at an exposure time of 10 min. These results clearly illustrate that, in air, linseed flax has much greater thermal stability than wheat straw, although both species exhibit a progressive increase in the rate of degradation as the exposure temperature is raised. After 30 min heating at 250 °C, both fibre types were found to be extremely friable, reflecting probable structural deterioration.

TABLE I Elemental composition of wheat straw and linseed flax straw fibres

Wheat straw		Flax straw	
Material	Elements	Material	Elements
Leaf	Moderate Si content S, K, Ca	Extruded	S, K, Ca, P, Cl, Cu, Trace of Si
Stem-outer surface	Highest Si content S, K, Ca	Non-extruded	S, K, Ca, Cl
Stem-inner surface	No Si Highest Ca content S, K	Shiv	S, K, P Least Ca

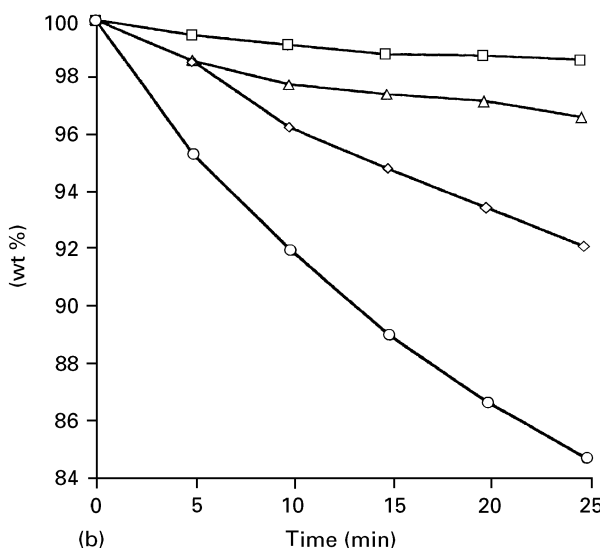
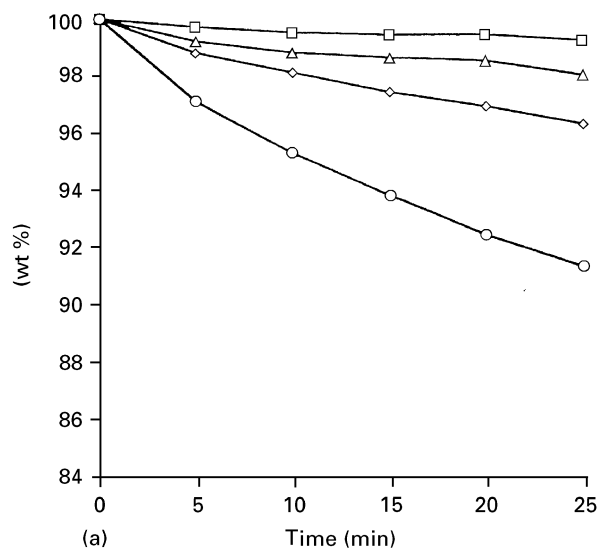


Figure 8 Isothermal gravimetric analysis of (a) linseed flax and (b) wheat straw in air; (□) 190 °C, (△) 210 °C, (◇) 230 °C, (○) 250 °C.

Figs 10 and 11 show TGA curves for flax and wheat straw in nitrogen and air environments obtained at a heating rate of 5 °C min⁻¹. Also included are results for lignin and α-cellulose.

Table II summarizes observations from these experiments including the magnitude of the initial weight loss (attributed to combined water), the residue remaining after heating to 725 °C and the onset of temperature for the main decomposition event.

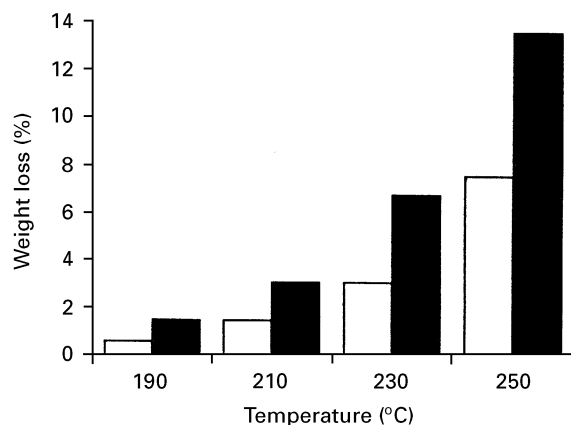


Figure 9 The effect of temperature on the weight loss from (□) flax straw and (■) wheat straw fibres (10 min exposure, in air).

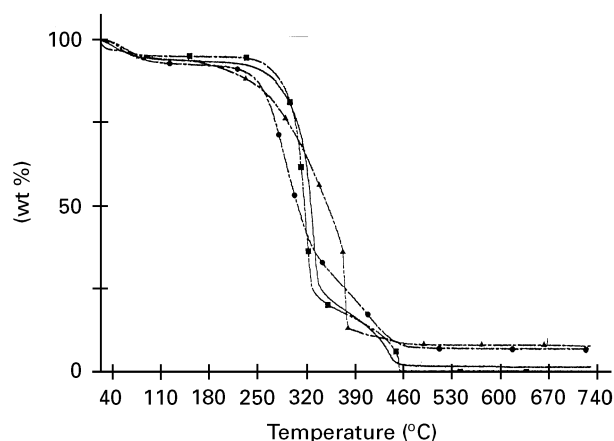


Figure 10 Thermogravimetric analysis of natural fibres and lignin in air, at a heating rate of $5^{\circ}\text{C min}^{-1}$. (■) α -cellulose, (▲) lignin, (●) wheat straw, (○) flax.

It is evident that both wheat and flax straw contain a significant level of water, which is released at temperatures well below that required when melt compounding with polypropylene, confirming the need to pre-dry these fibres prior to processing, or to employ devolatilization procedures during compounding to remove evolved steam. The thermal degradation of flax straw is very similar to α -cellulose in both air and nitrogen atmospheres, whereas the thermal behaviour of wheat straw lies between lignin and α -cellulose. Hence the lower thermal stability of wheat straw relative to linseed flax can be attributed to the higher lignin content of the former material.

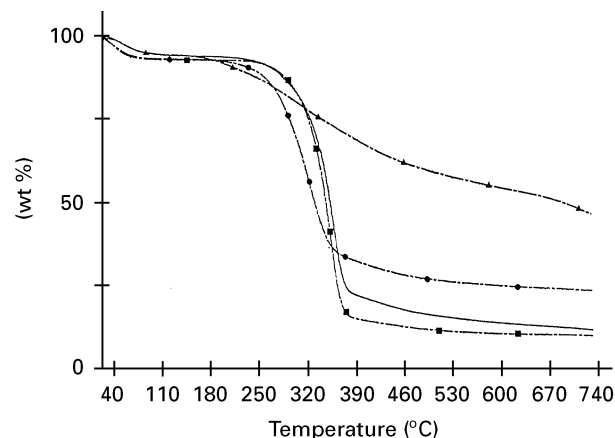


Figure 11 Thermogravimetric analysis of natural fibres and lignin in nitrogen, at a heating rate of $5^{\circ}\text{C min}^{-1}$. (■) α -cellulose, (▲) lignin, (●) wheat straw, (○) flax.

Thermal decomposition of cellulose has been widely studied on account of its combustibility [13]. Various products are derived on degradation, in particular levoglucosan, together with gaseous products, including H_2O , CO , CO_2 , H_2 and various volatile saturated and unsaturated hydrocarbons. Carbonaceous residues are also prominent in the $300\text{--}500^{\circ}\text{C}$ temperature range. When tested in air, α -cellulose was found to leave no residue at temperatures above 500°C , indicating that all products of decomposition have been oxidized, whereas in nitrogen nearly 10% of carbonaceous residue remains (Figs 10 and 11). Residue remaining after analysis of flax and wheat straw in air therefore reflects the extent of inorganic matter in these materials. The value of 7% obtained from wheat straw is consistent with reported silica levels typically contained in this fibre [14].

It is necessary to consider the mechanical properties of naturally occurring fibres under conditions which relate, as closely as possible, to their thermal history experienced during polymer processing. To this end, property measurements were made at test temperatures of up to 200°C . In addition, the effect of fibre gauge length on properties was assessed. Results are presented in Tables III and IV and analysed to assess the statistical significance of differences between means (represented as percentage error values). Very high standard deviations were observed in all cases, which is to be expected due to the inhomogeneous form of naturally occurring fibres and

TABLE II Summary of thermal analysis results from natural fibres and lignin

Material	Atmosphere	Moisture (wt %)	Residue at 725°C (wt %)	Main decomposition temperature ($^{\circ}\text{C}$)
Flax	Nitrogen	6.3	11.9	330
	Air	6.5	1.6	320 (421)
Wheat straw	Nitrogen	7.3	24.2	283
	Air	7.8	7.0	264
α -cellulose	Nitrogen	7.6	9.8	322
	Air	5.4	0	305 (449)
Lignin	Nitrogen	5.8	32.8	213
	Air	6.4	7.7	255

TABLE III Mechanical properties of wheat and flax straw fibres. The effects of temperature and sample gauge length on properties

Mechanical properties	No.	Temperature (°C)	Gauge length (mm)	Flax fibres	Wheat straw fibres
<i>E</i> -modulus (GPa)	1	25	20	12.5 (5.6)	3.6 (0.9)
	2	100	20	10.3 (6.0)	3.1 (1.4)
	3	200	20	8.2 (4.6)	2.8 (0.7)
Tensile strength (MPa)	1	25	20	134.0 (90.1)	49.5 (24.1)
	2	100	20	79.5 (49.4)	37.5 (19.0)
	3	200	20	52.5 (40.7)	45.7 (16.3)
<i>E</i> -modulus (GPa)	4	25	10	9.9 (4.0)	4.1 (1.2)
	5	25	15	8.1 (2.1)	5.1 (0.8)
	6	25	20	12.5 (5.6)	3.6 (0.9)
Tensile strength (MPa)	4	25	10	148.5 (52.1)	127.5 (25.9)
	5	25	15	146.9 (81.5)	97.9 (25.5)
	6	25	20	134.0 (90.1)	49.5 (24.1)

TABLE IV Mechanical properties of wheat and flax straw fibres. Statistical analysis of mechanical property data

Statistical analysis	Test	Flax fibres (% error)	Wheat straw (% error)
<i>E</i> -modulus for different temperatures	1, 2	15	14
	1-3	1	0
	2, 3	19	27
Tensile strength for different temperatures	1, 2	1	5
	1-3	0	29
<i>E</i> -modulus for different gauge lengths	2, 3	9	-
	4, 5	3	-
	4-6	-	11
Tensile strength for different gauge lengths	5, 6	-	0
	4, 5	48	1
	4-6	27	0
	5, 6	34	0

the predominance of defects within their structures. However, it was surprising to find that, in general, results obtained from wheat straw fibres were less variable than flax straw, because microstructurally the latter appeared to have a more homogeneous structure. As mentioned earlier, because of difficulties encountered during measurement of fibre diameter, assumptions were made during the determination of cross-sectional area, which may also have contributed to the apparent variability of properties.

It can be concluded from these results that under all test conditions, the linseed flax straw was significantly stronger and stiffer than wheat straw. The tensile strength and elastic modulus of flax straw decreased noticeably with increasing temperature up to 200 °C, which occurred to a lesser extent with wheat straw. There was no clear relationship between specimen gauge length and elastic modulus for either fibre type tested; however, the tensile strength of flax straw was found to be less dependent on gauge length than wheat straw, which increased markedly as gauge length was reduced.

Results obtained from the thermogravimetric analysis of these fibres provide some insight into the relationship between elastic modulus and temperature. Lignin which is known to contribute to the stiffness of the fibres begins to degrade at around 214 °C. Hence heating the fibres to 200 °C would be

expected to cause some softening, leading to a lowering in modulus.

The effects of moisture must also be considered. Although the fibres were pre-conditioned in a desiccator prior to testing, it was expected that they would still contain some constitutional tightly bound water. Furthermore, due to their hygroscopic nature, some moisture absorption immediately prior to testing was unavoidable. Hence it can be assumed that fibres tested at 25 °C contain some residual water which, to some extent, will evaporate at 100 °C. In the case of flax fibres, it is known that the presence of water increases stiffness and strength [15]. It was observed that, especially with flax straw fibres, tensile strength decreased with increasing test temperature. This effect has also been reported with sisal fibres and was explained in terms of differences in coefficients of thermal expansion between cellulose, hemicellulose, lignin and pectin [16]. As a consequence, at elevated temperatures the mismatch in expansion between structure-forming components of the fibre creates regions of stress concentration and possibly voids or flaws, resulting in weakening of the fibre. Thermal degradation of fibre components will exacerbate this problem.

There appears to be a distinction between the effects of specimen gauge length on strength and modulus for the two fibre variants, because results suggest that flax fibres are less sensitive to gauge length than wheat straw. It is expected that the longer the fibres, the higher will be the probability of finding defects with a critical size to initiate failure. However, it is known that in flax fibres, the average cell length is 8–30 mm compared to about 1.4 mm for wheat straw fibre cells. Hence, in a given specimen length there are more potential weak points at cell interfaces in wheat than in flax straw. Furthermore, from microstructural examination it can be seen that the cell wall in flax fibres contains many microfibrils which would limit the tendency towards total failure under stress from the presence of surface or even small internal defects.

Curves showing typical force/strain behaviour of the fibres under investigation are shown in Fig. 12. Many of the flax fibres gave two force peaks before total failure with the slope of the curve towards the second peak being lower than the first. This is typical of the failure mode of multiphase composite materials

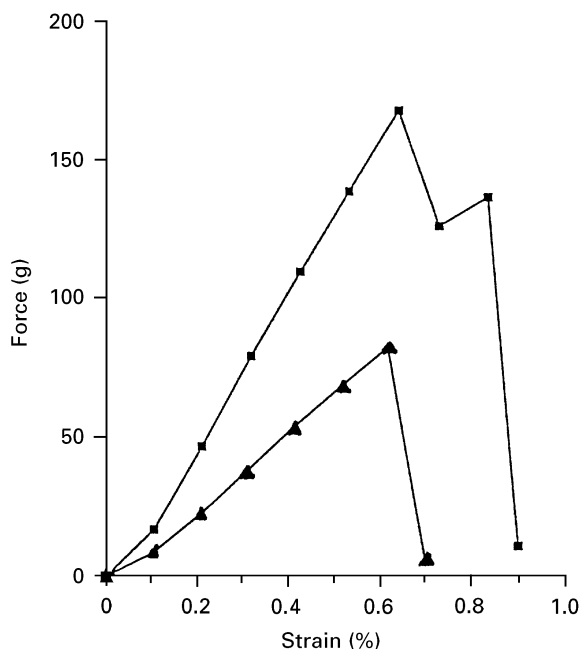


Figure 12 Force-strain curves for (■) flax and (▲) wheat straw fibres.

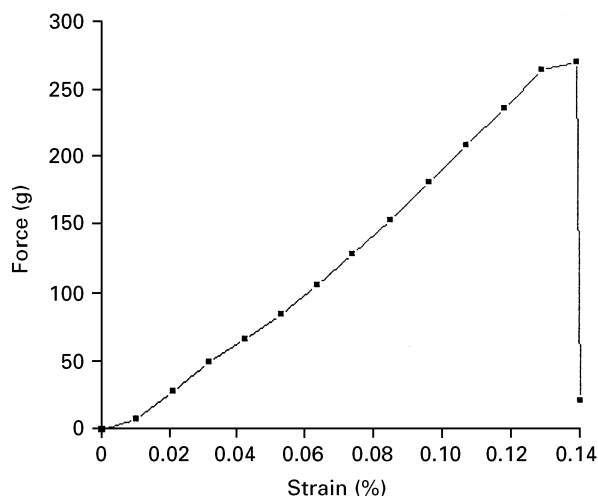


Figure 13 Force-strain curve for linseed flax fibre showing strain-hardening effect.

and is a reflection of the layered wall structure within this material.

It was also apparent that force-strain curves for several of the flax samples showed curvature towards higher force levels with increasing strain (Fig. 13). This phenomenon, which was not seen with wheat straw, is indicative of strain-hardening, which has also been reported with other natural fibres, such as coir [17]. It is conceivable that microfibrils present in the cell walls which are aligned off-axis in the unstrained fibre, progressively become reoriented in the axis of tension as stress is applied, resulting in increased fibre stiffening.

4. Conclusions

SEM and EDAX have revealed significant microstructural differences between the flax and wheat straw fibres investigated. The form of wheat straw used in this work appeared much more cellular than linseed

flax, which showed greater fibrous character and a higher aspect ratio. The flax fibres had a well-defined cross-sectional geometry and contained features resembling dislocations, clearly evident along their length. The surface region, or epidermis, of the wheat straw was particularly rich in silica, estimated by TGA to be around 7% by weight.

TGA demonstrated that both fibre types are prone to significant weight loss on exposure to temperatures up to 200 °C. Whilst this is, in part, due to release of adsorbed or constitutionally bound water, prolonged heating results in structural breakdown and extensive degradation of the organic phase. Linseed flax was found to be significantly more thermally stable than wheat straw, which is a consequence of the greater lignin content of the latter.

Micromechanical tests showed that flax was significantly stiffer and stronger than wheat straw, although these properties declined noticeably with increasing temperature. There was no clear relationship between gauge length and elastic modulus for either of the fibre types; however, the tensile strength of wheat straw fibres increased as gauge length was reduced.

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