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Mechanical properties of alkali treated plant fibres and their potential as reinforcement materials. I. hemp fibres

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In this study a thorough analysis of physical and fine structure of hemp fibre bundles, namely surface topography, diameter, cellulose content and crystallinity index, have been presented. The fibre bundles have been alkalised and physical and mechanical properties analysed. Alkalisation was found to change the surface topography of fibre bundles and the diameter decreased with increased concentration of caustic soda. Cellulose content increase slightly at lower NaOH concentrations and decrease at higher NaOH concentrations. The crystallinity index decrease with increase in caustic soda concentration up to 0.24% NaOH beyond which, it decreases with increase in NaOH concentration. It was also found that the tensile strength and stiffness increases with increase in the concentration of NaOH up to a limit. Tensile strength and Young's modulus increase with decrease in cellulose content, while crystalline cellulose decreases slightly but with improved crystalline packing order resulting in increased mechanical properties. Similar observations are elucidated by the crystallinity index. Alkalised hemp fibre bundles were found to exhibit a similar specific stiffness to steel, E-glass and Kevlar 29 fibres. The results also show that crystallinity index obtained following alkalisation has a reverse correlation to the mechanical properties. Stiffer alkalised hemp fibre bundles are suitable candidates as reinforcements to replace synthetic fibres. The improvement in mechanical properties of alkali treated hemp fibre bundles confirms their use as reinforcement materials.

1. Introduction

The strength of plant fibres is attributed to the rigidity and high molecular weight of cellulose chains, intermolecular and intramolecular hydrogen bonding and fibrillar and the crystalline structure of the fibres [1]. The strength and stiffness of fibres have also been shown to be dependent on the crystallinity index and micro-fibril angle. McLaughlin and Tait [2] have showed that strain is more dependent on the micro-fibril angle and that it increases with increase in the micro-fibril angle. Fibres with higher cellulose content have also been found to be stronger than those with low cellulose content as long as their micro-fibril angle is small. Table I [3–5] shows physical and mechanical properties of hemp fibre. The mechanical properties were derived in tension.

For instance, cotton with a micro-fibril angle between 20–30 and cellulose content of over 90% exhibits inferior mechanical properties to hemp and flax fibres, which have micro-fibril angles of less than 5° and cellulose content of over 80%. The above-mentioned characteristics make the fibres attractive materials for end uses such as reinforcements for polymeric materials.

The mechanical properties reflect the orientation of the micro-fibrils, which are inclined at an angle to the cell axis. It is worth mentioning that fibrous materials are commonly subjected to the following deformations: tension, compression, bending, torsion, shear, abrasion, wear and

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TABLE I Physical and mechanical properties of hemp fibre

Properties	Values
Length (ultimate) (mm)	8.3–14
Diameter (ultimate) (μm)	17–23
Aspect ratio (length: diameter)	549
Specific apparent density (gravity)	1500
Microfbril angel (θ)	6.2
Moisture content (%)	12
Cellulose content (%)	90
Tensile strength (MPa)	310–750
Specific tensile strength (MPa)	210–510
Young's modules (GPa)	30–60
Specific Young's modulus (GPa)	20–41
Failure strain (%)	2–4

flexing [6] whilst in the plant source or in use following extraction from the plant.

1.1. Modelling the stiffness of the cellulose cell wall

There is a strong correlation between the micro-fibril angle and the Young's modulus of the fibres. Models indicate that fibre stiffness is influenced by the spiral angle of the crystalline fibrils as well as the concentration of non-crystalline materials [7]. These structural parameters vary between the different types of natural fibre accounting for some of the variations in reported fibre properties. The effect on the mechanical properties of increased micro-fibril angle plays an important role when determining the mechanical properties of fibre-reinforced composites. It is necessary to measure the alignment of micro-fibrils applied to plant fibres to the direction of the force especially in determining tensile properties, bearing in mind that plant fibres exhibit significant mechanical anisotropy. A theoretical analysis of the way a fibre behaves when stretched may in practice represent the behaviour of fibre-reinforced composites when determining their mechanical properties. In this case a uniform strain theory has been used to obtain an estimate of the stiffness of the entire arrangement in both the fibre and the cell wall composite material. The theory uses an assembly of springs tied together so that they all receive the same displacement μ under a tensile load F as shown in Fig. 1. The theory is based on the work of Bodig and Jayne [8].

$\bar{\mu}$ and $\bar{F}$ is the mean displacement and load on the micro-fibrils respectively. K_1 and K_2 are the micro-fibril constants.

Let F be the load and μ the displacement under tension. The total force necessary to produce the displacement is the sum of the forces in the fibre, F_f, applied to the crystalline and amorphous regions (Equation 1).

$$F_f = F_c + F_{nc} \tag{1}$$

Where, F_c and F_{nc} represents the forces applied to the crystalline and non-crystalline materials respectively. The

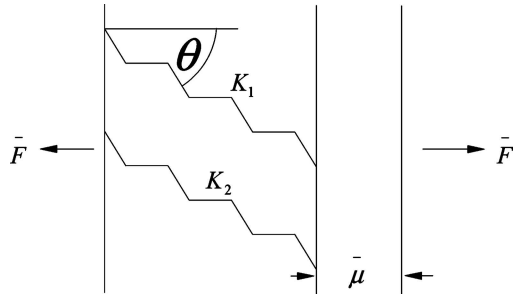


Figure 1 Arrangements of a uniform elastic deformation model in the plant fibre cell wall.

stiffness (Equation 2) of the array is given as:

$$k = \frac{F}{\mu} = \sum K_i \tag{2}$$

The components in Fig. 1 are at an angle θ to the direction of the force applied. A displacement $\bar{\mu}$ is applied in the direction of the applied force $\bar{F}$. The forces, which appear in each spring element representation, are obtained from the product of the stiffness and the component of the displacement that is parallel to their orientation (Equation 3).

$$\overline{F_i} = K_i \bar{\mu} \cos\theta_i \tag{3}$$

The total force in the longitudinal direction of the fibre necessary to cause this displacement is the sum of the longitudinal forces on each crystallite (Equation 4).

$$\overline{F} = \sum F_i \cos\theta_i \tag{4}$$

Substituting F_i from above gives Equation 5

$$\overline{F} = \bar{\mu} \sum k_i \cos^2\theta_i \tag{5}$$

The overall stiffness of the system of the fibre in the fibre axis is given by Equation 6.

$$\overline{k} = \sum K_i \cos^2\theta_i \tag{6}$$

If: $\overline{k}$ = overall stiffness of the fibre (E_f) and K_i is the stiffness of the micro-fibrils (E_S) then Equation (6) becomes (7).

$$E_f = E_S \cos^2\theta \tag{7}$$

Equation 7 gives the longitudinal Young's modulus of plant fibres measured in tension. Efforts are being made to determine the transverse Young's modulus of plant fibres but this is not covered here. However, Cichocki and Thomason [9] used an environmental scanning electron microscopy (ESEM) equipped with a load frame to measure the Young's modulus of a carefully sectioned array of

wood cells in the transverse direction. Their measurement indicated that the transverse Young's modulus varied with the type of wood used and was less than the longitudinal Young's modulus [9].

1.2. Modelling of the cell wall as a composite material

Since both the crystalline and non-crystalline region will deform, the applied load is shared between these two components just as is the case with the composites. The determination of stiffness properties of plant fibres can be predicted by using the rule of mixtures (ROM). For instance, Equation 7 is used to estimate the stiffness or modulus of elasticity of the plant fibre cell wall [8] along the fibre axis. The effective modulus of the fibre (E_f) is given in terms of the amounts of participating components present in the fibre. The ROM takes into consideration the masses of the crystallites and non-crystallites to determine the stiffness of the composites (Equation 8).

$$E_f = V_c E_c \cos^2\theta + V_{nc} E_{nc} \tag{8}$$

Where, E_c and E_{nc} are the moduli of crystalline and non-crystalline regions and V_c and V_{nc} are the volume fractions of crystalline and non-crystalline regions. Kulkarni *et al*. [10] reported elastic moduli of the crystalline and non-crystalline regions for vegetable fibres as 45 GPa and 3 GPa respectively. When banana fibre was tested at a micro-fibril angle of 12° and 11°, with a fibre diameter of 100 μm with volume fractions of 0.65 and 0.35 for crystalline and non-crystalline components respectively, the modulus values obtained using Equation 8 compared well with the practical modulus values obtained by Kulkarni *et al*. [10] when determining the mechanical properties of banana fibres *Musa sepientum*. Mukherjee *et al*. [11] performed similar work on sisal fibre tested at different test gauge lengths and speeds and the results obtained were comparable to the theoretical predictions.

1.3. Fibre modifications

Plant fibres must exhibit a compatible surface morphology for the development of a coherent interface with matrix polymers but because of the surface impurities present in plant materials the development of a good fibre-matrix interface is impaired. However, in order to make use of the good physical and structural characteristics of the fibres they are treated with chemicals such as caustic soda to modify surface topography and the fine structure. The main requirement for reinforcement is to use stiff fibres and a well-bonded fibre-matrix interface with the ultimate aim of reaching the stiffness of conventional synthetic reinforcement such as carbon and glass fibres. In plant fibres these requirements are partially attained by alkali treatment.

Hemp fibres possess surface impurities such as wax and natural oils and sometimes processing oils can also be deposited at the surface. Bleaching and/or scouring using solvents can remove these surface impurities. Several fibre modification processes in textile manufacturing require the removal of these surface impurities to improve lustre and dye uptake. In composite manufacture removal of surface waxy materials improves mechanical interlocking and reactivity with the resins thus developing strong interfacial adhesion. Cellulose forms the main structural constituent of plant fibres and contributes immensely to the mechanical properties of plant fibres. Other components such as lignin and hemicelluloses play an important part in the characteristic properties of the fibres. Toughness, that is the tendency of plant fibres to absorb energy in impact, is decreased with a decreasing amount of lignin and/or hemicelluloses while at the same time the strength and stiffness of the fibre is increased up to a limit. The development of fibre-reinforced composites favours the use of stiff fibres for reinforcement of polymeric materials.

Removing lignin and hemicelluloses thus leaving stiffer cellulose can produce stiff plant fibres. The removal of hemicelluloses leaves a less dense and less rigid interfibrillar region allowing the fibrils to re-arrange along the fibre major axis [12]. Stretching the fibre results in better load sharing by the fibrils hence higher stress development in the fibre. On the other hand, softening of the interfibrillar matrix adversely affects the stress transfer between the fibril and thereby the overall stress development in the fibre under tensile deformation. Removing the lignin makes the middle lamella joining the ultimate cells become more plastic and homogeneous due to the gradual elimination of micro-voids whereas the ultimate cells themselves are only slightly affected. The rearrangement of the fibrils along the fibre axis and the resulting homogeneity of the ultimates lead to a packing order with increased crystallinity index for the plant fibres. Physical methods such as heating/drying can be applied to plant fibres to remove hemicelluloses, which are sensitive to high temperatures. The steam explosion technique is another method commonly used to produce clean fibres. Several chemical methods have been applied to modify plant fibres and these are discussed in the following sections together with physical methods.

In this work hemp fibre bundles that have been alkalised have been tested in tension and the results compared with conventional synthetic fibre reinforcements to assess the potential of hemp fibre as an alternative to synthetic fibres. Also, the theoretical stiffness of plant fibres has been predicted and results compared with experimental values.

2. Experimental methods

2.1. Materials

Hemp fibre used in this work was kindly supplied by the Hemcore Company Limited of United Kingdom. No specifications were available regarding the physical characteristics of the supplied fibres such as staple length, density, diameter and processing conditions. Sodium hy-

droxide pellets of 98% strength and glacial acetic acid were supplied as general laboratory reagents.

2.2. Fibre preparation

Fibres were stored in a conditioning chamber containing a saturated sodium nitrite solution whereby 85 g of the solute was added to 100 cm^3 of water. For a room temperature of 20 ± 2°C, the conditioning chamber with the solution in it generates a relative humidity inside the chamber of 65 ± 2% relative humidity.

2.3. Alkali treatment

Hemp fibre bundles were soaked in beakers containing 0.03%, 0.08%, 0.16%, 0.24%, 0.32% and 16% weight by weight (w/w) concentrations of caustic soda (NaOH) and placed in a water bath controlled at 20 ± 2°C for 48 h. The 16% NaOH was used to study the effect of extreme concentration of caustic soda on fibres. The fibres were then removed, washed with distilled water containing 1% acetic acid, to neutralise excess sodium hydroxide, and then thoroughly rinsed with distilled water. The fibres were then dried to remove free water and placed in a glass container in a conditioning chamber.

2.4. Determination of fibre diameter

Twenty-five fibre specimens each 20 mm long were cut and prepared for SEM examination. The SEM micrographs prepared were then subjected to image analysis and their diameter determined along the width of the fibre bundles. Fifty readings were recorded for each fibre specimen and the mean, standard deviation and standard error were calculated.

2.5. Determination of the cellulose content of fibres by density methods

The cellulose content of plant fibres was calculated using a combination of the bulk, absolute and cellulose densities using Equation 9. A full description of the way densities were determined is provided in our earlier publications [13] and will not be repeated in this paper.

$$Z = \left[2\left(\frac{\rho_b}{\rho_a} + \frac{\rho_a}{\rho_{cell}}\right) - \frac{\rho_b}{\rho_{cell}} - 2\right]100 \qquad (9)$$

Where ρ_a, ρ_b, ρ_{cell} and Z are the absolute, bulk (apparent), cellulose densities, and cellulose content respectively.

2.6. Tensile test

The Instron tensile tester, model 1122, was used. The instrument incorporates a highly sensitive electronic load weighing system, with load cells employing strain gauges

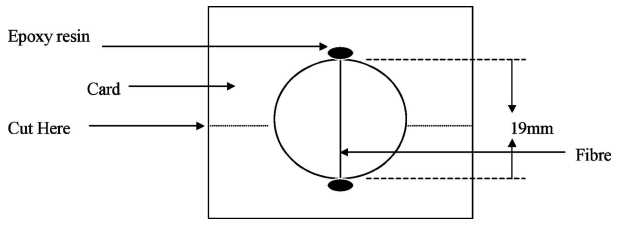


Figure 2 Mounting card of a fibre test piece.

to detect the load applied to the specimen under test. For single ultimate fibres the most sensitive load cell is that with a capacity of 0.5 N. However, because what were being tested are bundles of fibres in the case of hemp fibre a load cell with a sensitivity of 10 N was employed. This was calibrated by hanging a 1-kg weight on the upper jaw. With the pen switched on, the pen moves to full-scale deflection and to acquire the highest sensitivity it was multiplied by a factor of ten. It was then adjusted to 9.81 divisions on the chart to compensate for the conversion of the gramme weight to load in newtons. The pen was then switched off and the calibration weight was removed. The gripping jaws were adjusted to the length of the card. The crosshead speed was adjusted to give a standard time to break of about 20 s. The chart speed was adjusted to give a reasonably sized deflection on the chart paper.

Fibres were temporarily fixed on the card by adhesive tape across a circular-hole of 19 mm diameter cut in a card. Fig. 2 shows a cross-sectional view of the mounting card of a fibre test piece. A 'blob' of epoxy resin was dropped on the edge on both sides of the centre of the hole along the length of the card. In order to let the epoxy resin set, the whole set-up was left in the conditioning chamber for 48 h before testing.

The card was placed between the Instron jaws and a pair of scissors was used to cut both sides of the card as shown in Fig. 2 to start testing. Thirty-two specimens were considered sufficient for each test. The mean ultimate tensile strength, mean breaking strain and extension per cent, the mean Young's modulus and the respective standard deviation were determined. However, for comparing different fibres, the value of specific stress at break is used and is called specific strength or tenacity. For use in comparing strengths on the basis of area of cross-section, the stress at break is termed the ultimate tensile stress. Tests for the tensile strength of the 16% NaOH treated hemp fibre bundles were not performed due to the crimpy nature of the fibres following caustic soda treatment.

3. Results and discussion

3.1. Surface topography and transverse sections

SEM micrographs of hemp fibre bundles are shown in Figs 3–5 and they comprise bundles of individual cells that have been bound together by lignin-rich, weak intermolecular bonds. To avoid repetitive descriptions three fibre specimen profiles have been used to elucidate the

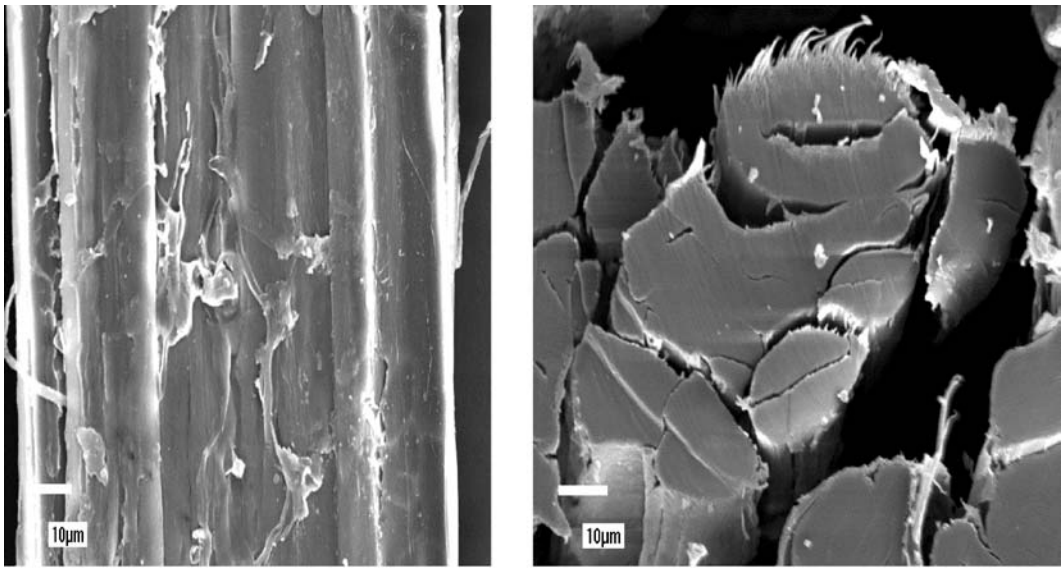


Figure 3 (a) Longitudinal and (b) cross sectional view of untreated hemp fibre.

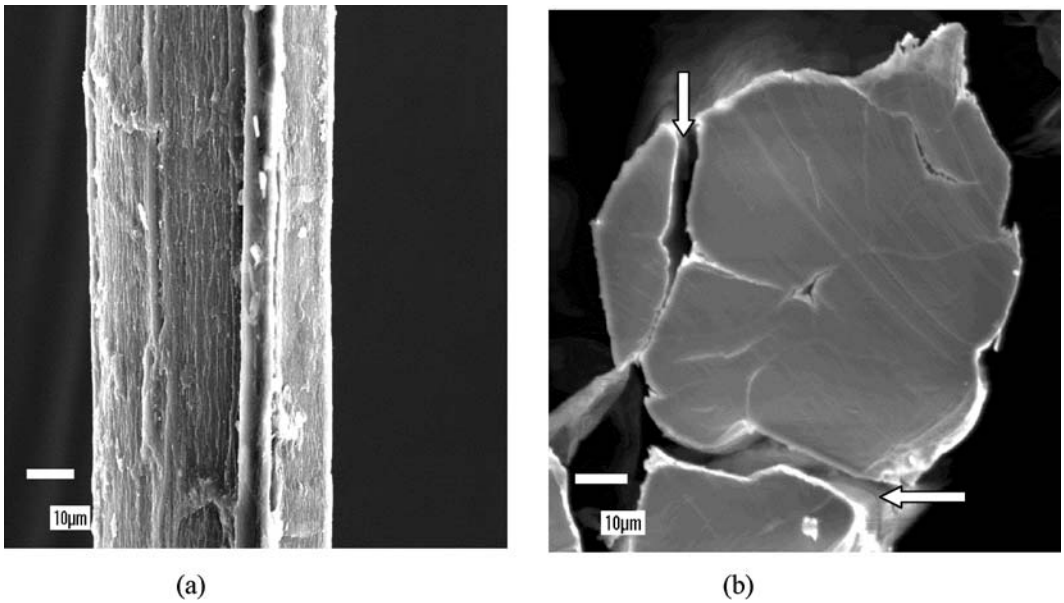


Figure 4 (a) Longitudinal and (b) cross sectional view of 0.24% NaOH treated hemp fibre.

effect of caustic soda on the hemp fibre cell namely the untreated, 0.24% NaOH and 16% NaOH treated hemp fibre bundles. Following alkalisation the surface topography of hemp fibre bundles is rougher than before treatment as shown in Figs 4 and 5 respectively. Mwaikambo and Ansell [14] reported similar results when studying the effect of chemical treatment of hemp, sisal, jute fibres bundles and kapok fibres.

The SEM micrograph of the longitudinal surface of untreated hemp fibre bundles (Fig. 3a) shows waxy, oily and possibly fibrous surface materials. Waxes and oils provide a protective layer to the fibres. A transverse section (Fig. 3b) shows fibre bundles one of which has a large lumen. The longitudinal view of 0.24% NaOH treated hemp (Fig. 4a) fibre shows a clean rough surface. Its surface topography is cleaner than the untreated fibre. The cross sectional view of 0.24% NaOH treated fibre shows a swollen fibre bundle with a small lumen (Fig. 4b). Two fibre bundles showed with an arrow (Fig. 4b) are starting to separate from a larger bundle as a consequence of alkalisation.

Fig. 5a shows longitudinal view of the 16% NaOH treated fibre bundles that are cleaner and are clearly, but not completely, separated into individual ultimate fibres. The two left ultimate fibres in Fig. 5a contains cracks along the fibre caused by the high concentration of caustic soda. Fig. 5b shows a cross sectional view of alkalised fibres revealing the ultimate fibres weakly held together

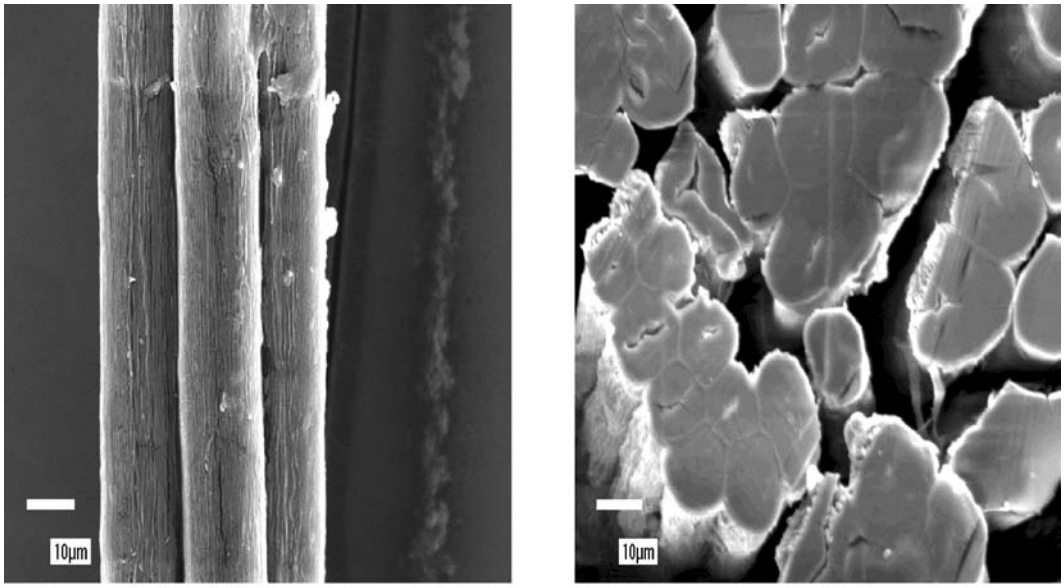


Figure 5 (a) Longitudinal and (b) cross sectional view of 16% NaOH treated hemp fibre.

possibly by pectin and lignin residues, and partially dissolved cellulose material.

More importantly, Fig. 5b reveals that even high concentrations of caustic soda do not effectively separate hemp fibre bundles into individual fibre cells. This also implies that caustic soda does not degrade and/or dissolve all the polymeric materials present in plant fibres mainly lignin and pectin, which function as natural cementing substances.

3.2. Structure-property relationship

Mwaikambo and Ansell [13] reported results for the diameter, cellulose content and amount of non-cellulose materials (largely lignin) in hemp fibre bundles. Following alkalisation they also reported [1] the crystallinity index (I_I), which closely represents the ratio of crystalline materials to amorphous cellulose in hemp fibres.

3.2.1. Effect of the fibre diameter

Following alkalisation the dependence of mechanical properties on the diameter of hemp fibre bundles is illustrated in Figs 6 and 7. The diameters of untreated and alkali treated hemp fibre bundles were determined. The tensile strength and bundle diameter were determined using the Instron tensile tester using SEM and image analysis techniques respectively.

The high strength and modulus (Figs 6 and 7) of small diameter fibre bundles is understandable since, in the limit, a single unbroken chain of cellulose molecules must be approaching the theoretical tensile strength of bonds between atoms. The relationship between strength and diameters for hemp fibre bundles is inversely parabolic.

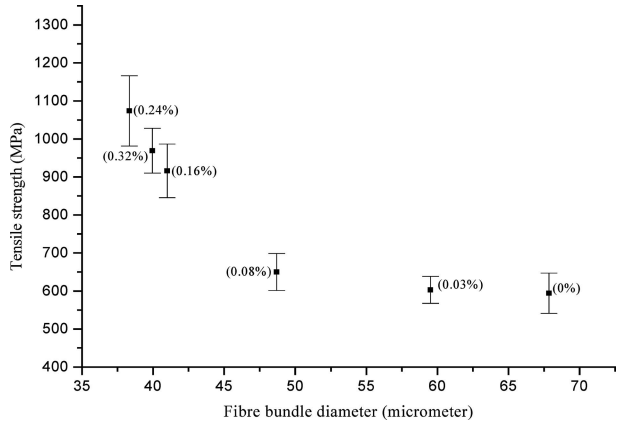


Figure 6 The strength of hemp fibre bundles with respect to fibre bundle diameter following caustic soda treatment.

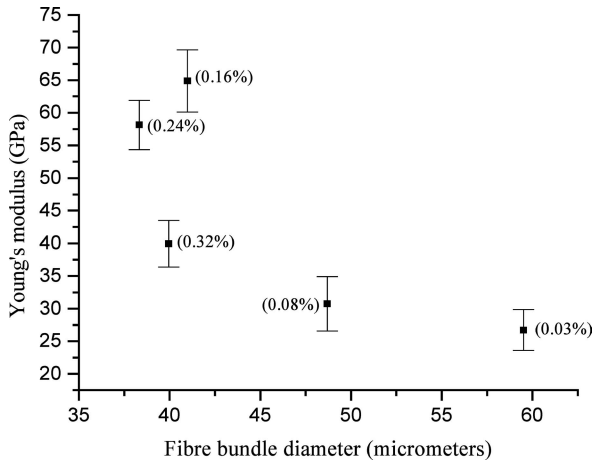


Figure 7 The Young's modulus of hemp fibre bundles with respect to fibre bundle diameter following caustic soda treatment.

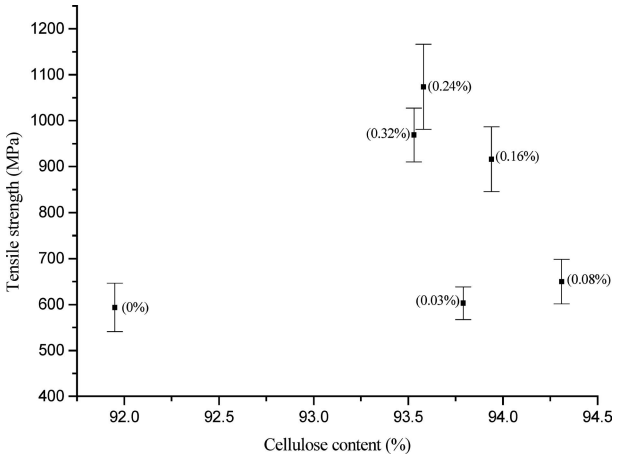


Figure 8 The tensile strength of hemp fibre bundles with respect to cellulose content following caustic soda treatment.

However, it is observed that the separation of ultimate fibres is optimised at around 0.24% NaOH (Fig. 6) and at 0.16%NaOH (Fig. 7) respectively. The drop in tensile strength and Young's modulus beyond 0.24%NaOH treatment is due to the degradative effect of caustic soda on the cell wall.

3.2.2. The effect of cellulose content

Fig. 8 and 9 shows the effect of cellulose content on the tensile strength and Young's modulus of alkalised hemp fibre bundles. Following a 0.08%NaOH treatment hemp fibre bundles exhibits an increase in cellulose content of about 3% that in turn induces an increase of tensile strength of about 2%. Further increase of caustic soda concentration results in a rapid increase reaching an optimum of about 81% increase in tensile strength at 0.24%NaOH. The slight increase in cellulose content is due the close compactness of the crystalline cellulose, thus making it difficulty for the NaOH molecules to penetrate the cell wall. However, the reduction in the cellulose content beyond 0.08%NaOH treatment is due to the degradation of the cell wall and increased amorphous cellulose material with improved crystalline packing resulting in increased tensile strength. Mukherjee *et al.* [11, 12] and Mwaikambo and Ansell [15, 16] reported the correlation of the increase in the amorphous cellulose following caustic soda treatment at the expense of a decrease in the crystalline cellulose. Further release in the strain occurs on the crystallites following alkalisation, which results in improved packing order along the longitudinal direction [7] of the fibre. A similar pattern is observed in Fig. 9 for the stiffness characteristics of alkali treated hemp fibre bundles.

3.2.3. The effect of crystallinity index

Following alkalisation of the hemp fibre bundles both the tensile strength (Fig. 10) and Young's modulus (Fig. 11) broadly decrease with increase in the crystallinity index. These results contradict the results reported by Gassan *et al.* [7], which shows that there was a strong correlation between the strength of alkali treated jute fibre bundles and crystallinity index also referred to as the crystallinity ratio. Gassan *et al.* [7] also concluded that changes in mechanical properties could be attributed to changes in crystalline orientation.

These two results contradict demonstrating that different plant fibre types exhibit different structure-property relationship. These differences in property between types of plant fibre reflect the variations in their fine structure, chemical constituents and the composite nature of the fibres. To substantiate the above statement results for the mechanical properties of sisal and jute fibre bundles subjected to the same caustic soda concentrations as those of hemp fibre bundles will be presented in future publications.

3.2.4. The effect of the micro-fibril angle

The initial postulated stiffness model of the micro-fibril inclined at an angle θ to the fibre major axis has been pre-

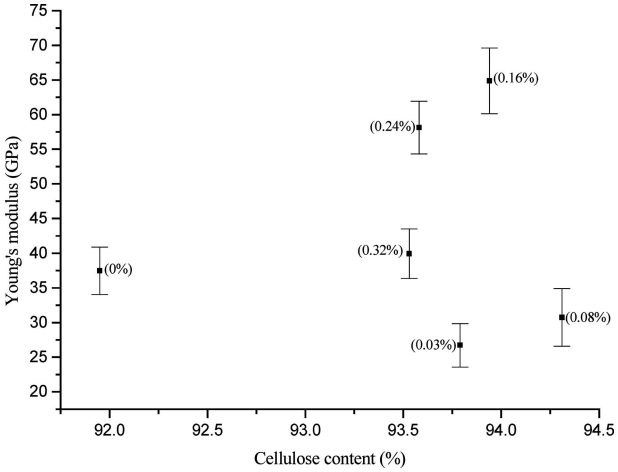


Figure 9 The Young's modulus of hemp fibre bundles with respect to cellulose content following caustic soda treatment.

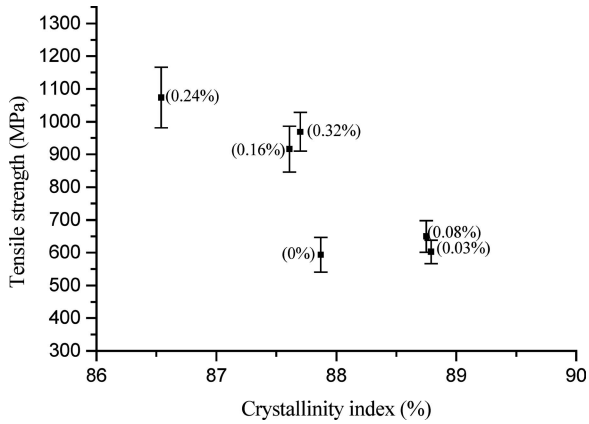


Figure 10 The dependence of tensile strength of hemp fibre bundles on the crystallinity index following caustic soda treatment.

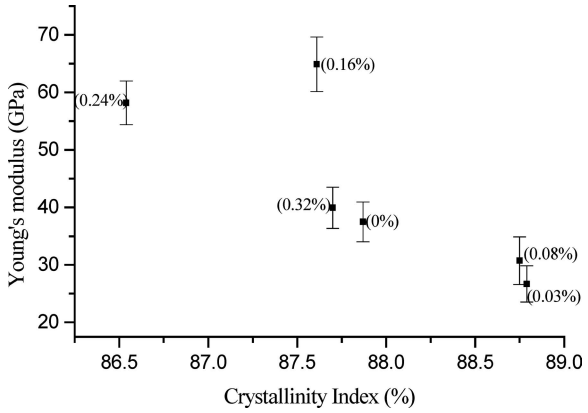


Figure 11 The dependence of Young's modulus of hemp fibre bundles on the crystallinity index following caustic soda treatment.

sented in Equation 7. The general equation for the stiffness of plant fibres is derived using the rule of mixtures and results in Equation 8. For the purpose of determining the micro-fibril angle of hemp fibre bundles Equation 8 is modified to obtain Equations 10 and 11.

$$E_f = V_S E_S \cos^2\theta + (1 - V_S)E_L \tag{10}$$

$$E_f = V_Z E_Z \cos^2\theta + (1 - V_Z)E_Z \tag{11}$$

Where E_f, V_S, E_S, and E_L, are the elastic moduli of the fibre, volume fraction and stiffness of micro-fibrils and the stiffness value for non-cellulose materials (represented mainly by lignin) respectively. V_Z and E_Z are the volume fractions and stiffness of cellulose content. The subscript S (Fig. 9) and Z (Fig. 10) represents the winding direction of micro-fibrils observed in plant fibres. Most plant fibres exhibits either an S or Z winding direction of micro-fibrils except for Cotton fibres, which exhibit both S and Z winding direction [6]. Using Equation 12 an estimate of the micro-fibril angle θ was determined.

$$\theta = \mathrm{Cos}^{-1}\sqrt{\left(\frac{E_f - (1 - V_S)E_L}{V_S E_S}\right)} \tag{12}$$

Only the micro-fibril angle of untreated fibres was determined (6.8°) and this is shown in Table II.

In order to evaluate the elastic moduli of the micro-fibrils it was assumed that following alkalisation (a) the micro-fibril angle and (b) the stiffness of the non-cellulose material remain the same. It is worth noting that caustic soda does not degrade lignin hence validating the second assumption. While the first assumption may not strictly be valid, combined with the second assumption acceptable results for the stiffness of the fibre and cellulose content in untreated and alkali treated hemp fibre bundles are obtained and are shown in Table II. Using the stiffness model of plant fibres (Equation 8) and the above physical and structural properties of hemp fibre bundles including the literature values of the stiffness of lignin, 3.0 and 3.4 GPa, reported by Kulkarni *et al.* [10] and McLaughlin and Tait [2] respectively, estimates of the elastic moduli of the micro-fibrils (E_S) were determined as a function of firstly crystallinity index (E_I) and secondly cellulose content (E_Z also taken as E_S) and are shown in Table III.

TABLE II Estimate of the mciro-fibril angles of untreated hemp fibre bundles as a function of cellulose content (Z)

Fibre type	Hemp
V_Z	0.9195
E_Z (GPa)	41.04
E_f (GPa)	37.48
θ (°)	6.8

TABLE III The stiffness of the micro-fibrils of hemp fibre bundles calculated as a function of crystallinity index (I) and cellulose content (Z)

Treatment (%NaOH)	0	0.03	0.08	0.16	0.24	0.32
E_I (GPa)	42.95	30.25	34.87	74.78	67.87	45.99
E_Z (GPa)	41.04	28.84	32.82	69.74	62.76	43.12

Table II indicates that E_f is lower than E_Z and that the calculated value for the micro-fibril angle of hemp fibre is about 9.7% greater than the literature value (Table I). The variation in the micro-fibril angle between calculated and literature value [5] is due to differences in the environmental testing conditions. E_S (Equation 13) and E_I (Equation 13) were obtained by substituting values of V_I, $E_f$and E_I, V_I respectively, the calculated θ and E_L in Equation 12.

$$E_S = E_Z\left[\frac{E_f - (1 - V_S)E_L}{V_S \mathrm{Cos}^2\theta}\right] \tag{13}$$

$$E_I = \left[\frac{E_f - (1 - V_I)E_L}{V_I \mathrm{Cos}^2\theta}\right] \tag{14}$$

Equations 13 and 14 were developed and used to determine the stiffness of the micro-fibrils with respect to the cellulose content and crystallinity index. Fig. 12 was used to illustrate the difference in the stiffness when the two parameters are applied. It was observed that at all the stages of the different caustic soda concentrations the E_I is higher than E_Z (E_S) implying that the use of crystallinity index provides a better structure-stiffness correlation on hemp fibres than cellulose content. This also implies that whereas, the cellulose content might decrease slightly when hemp fibre is subjected to caustic soda treatment, the crystallinity index and the amount of crystallites increase.

This method of determining the stiffness of the micro-fibril and crystalline material offers a new and more accurate route not reported before in any literature and it is easier and quicker to use. The micro-fibril angle used in this work was that calculated using untreated fibres. How-

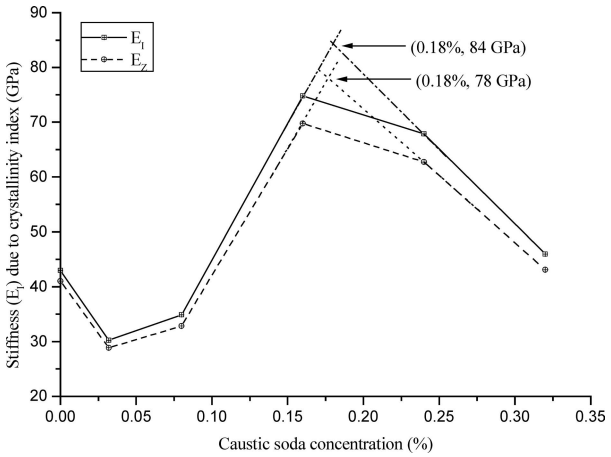


Figure 12 The stiffness of micro-fibrils of hemp fibre bundles with respect to crystallinity index and cellulose content.

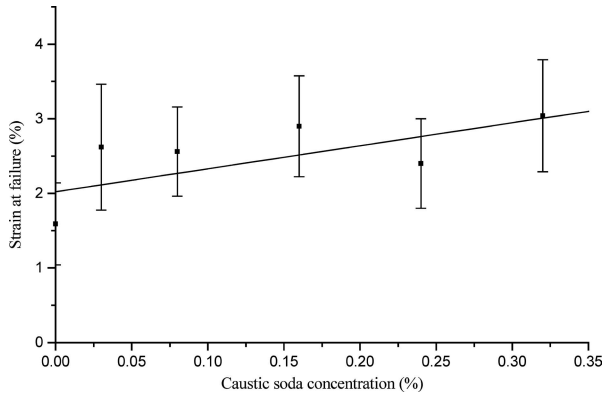


Figure 13 The effect of caustic soda on the strain of hemp fibre bundles tested in tension.

ever, it will change with changes in the concentration of caustic soda used to treat hemp fibres.

Table III shows that the elastic modulus (E_I) values of the crystalline material determined using the crystallinity index (Equation 14) are higher than values of elastic modulus (E_S) determined using the micro-fibril or cellulose content (volume fraction of cellulose) (Equation 13). This indicates that crystallinity index is a better measure of the plant fibre's stiffness than cellulose content.

The results also show that the lower stiffness values obtained using the cellulose content is a result of the presence of tiny air pockets [14] and the lignin content and hemicelluloses which reduce stiffness. The stiffness values obtained in Table III are close to stiffness values obtained by McLaughlin and Tait [2] and Kulkarni *et al.* [10] using bowstring hemp (*Sansevieria metallica* Géróme and Labroy) and banana (*Musa sepintum*) fibres respectively.

3.3. Tensile properties of hemp fibre bundles

The effect of alkali treatment on the mechanical properties of hemp fibre bundles was studied. The nature and texture of the fibre bundles are not the same in their natural or alkalised states. For instance, the average diameter and density of the untreated and alkali treated hemp fibre bundles have previously been found not to be the same [17]. These factors will affect the mechanical properties of the fibres, which exhibit large variations in mechanical properties. The mechanical properties of the fibres are given in Table IV.

The mechanical properties shown in Table IV are illustrated using Figs. 13–15. The elongation at break of untreated hemp fibre bundles (Table IV and Fig. 13) is less than the alkalised fibres due to the plasticisation of the cellulose in the cell wall, which might be caused by the presence of water molecules in the open cell wall structure. Fig. 13 shows the strain at failure of untreated and alkali treated hemp fibre bundles tested in tension.

The overall picture shows an increase in strain with increase in the concentration of caustic soda (Fig. 13) indicating that the cell wall degraded as the non-cellulose materials are removed following alkalisation. The increase in tensile strain at failure with increase in the concentration of caustic soda ultimately correlates with a decrease in tensile strength and Young's modulus of alkali treated hemp fibres. This implies that the correlation between the mechanical properties of hemp fibre bundles with the changes in the crystallinity index with respect to the changes in the concentration of caustic soda is directly related to the changes in the strain.

Fig. 14 show the tensile strength of untreated and alkalised hemp fibre bundles, which show a gradual increase in tensile strength with increase in the concentration of caustic soda up to 0.08% NaOH. Beyond this concentration the strength increases sharply and reaches a maximum at 0.24% NaOH and then falls. Fig. 15 shows the Young's modulus of untreated and alkali treated hemp fibre bundles. Unlike the results for the tensile strength, Young's modulus decreases slightly with increase in concentration of caustic soda, but rises sharply between 0.08% and

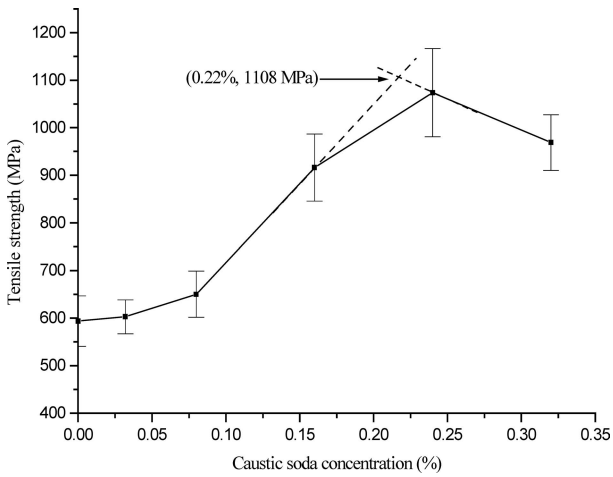


Figure 14 Tensile strength of untreated and alkalised hemp fibre bundles with respect to caustic soda concentration.

TABLE IV Tensible properties of untreated and alkalised hemp fibre bundles

Treatment (%NaOH)	Tensile strength (MPa)	Specific tensile strength (MPa)	Young's modulus (GPa)	Specific Young's modulus (GPa)	Strain at failure (%)	Specific gravity
0	593.72 (105.96)	403.62	37.48 (3.44)	25.48	1.59 (1.10)	1.471
0.03	602.75 (71.08)	402.37	26.72 (3013)	17.84	2.62 (1.69)	1.498
0.08	649.96 (96.64)	431.58	30.74 (4.17)	20.41	2.56 (1.20)	1.506
0.16	916.14 (141.27)	610.35	64.88 (4.75)	43.22	2.90 (1.35)	1.501
0.24	1073.72 (185.36)	717.73	58.14 (3.79)	38.86	2.40 (1.20)	1.496
0.32	968.95 (117.50)	648.13	39.94 (3.55)	26.16	3.04 (1.50)	1.495

Figure in brackes are standard deviation at 95% confidence level.

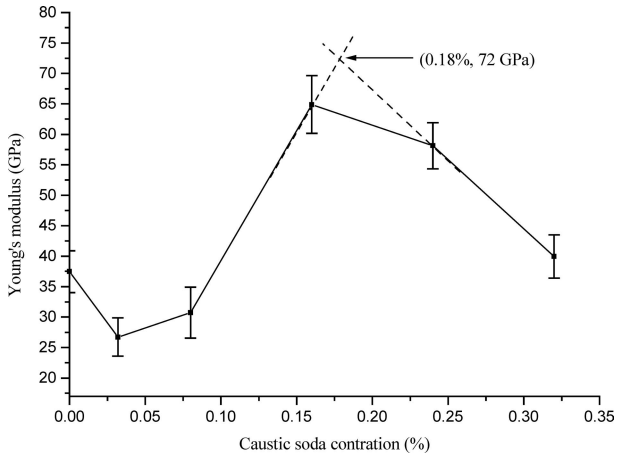


Figure 15 Young's modulus of untreated and alkalised hemp fibre bundles with respect to caustic soda concentration.

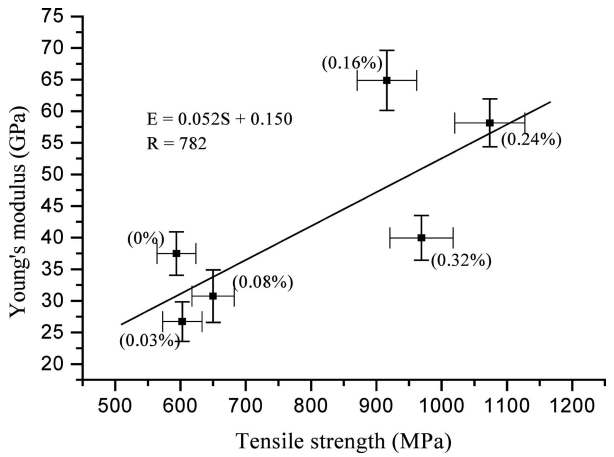


Figure 16 Tensile strength vs Young's modulus of hemp fibre bundles following caustic soda treatment.

0.16% NaOH beyond which the fibres exhibit a gradual decrease in the Young's modulus.

The property trends for the tensile strength (Fig. 14) are quite similar to the trends in Young's modulus (Fig. 15) with optimum performance attained at caustic soda concentration of 0.24% and 0.16% respectively. However, extrapolated values are 0.22%NaOH exhibiting a tensile strength of 1108 MPa, which is higher than the experimental value (1073 MPa). This implies that a follow up of the effect of NaOH concentration taken at close range on the tensile strength and Young's modulus of hemp fibre bundles will result in values that are closer to the extrapolated values (Figs 14 and 15 respectively). The variations in the concentration of caustic soda at which optimum mechanical properties are attained are due to changes in fine structure following alkalisation and experimental conditions.

The Young's modulus versus tensile strength of hemp fibre bundles has been plotted and is shown in Fig. 16. A regression line through the data points is shown and an equation (Fig. 16-inset) has been provided where E and S indicates Young's modulus and tensile strength respectively and R is the coefficient of correlation. The linear relationship of the plots illustrates the theoretical model available in literature [16–18].

The variation of the scatter of the points (Fig. 16) is not significant indicating good test control and that the fibre's weak places, which would result in stress concentrations, are evenly distributed and minimal.

The property-to-weight ratio expressed as the specific strength, σ_s, and specific modulus, E_s (Fig. 17), that is the ratio of strength and modulus to specific gravity are important properties of fibres, especially where low mass is essential [18]. They are particularly useful parameters when transporting bulky materials.

The relationship between the specific strength and specific modulus (Fig. 17) is linear and increases with in-

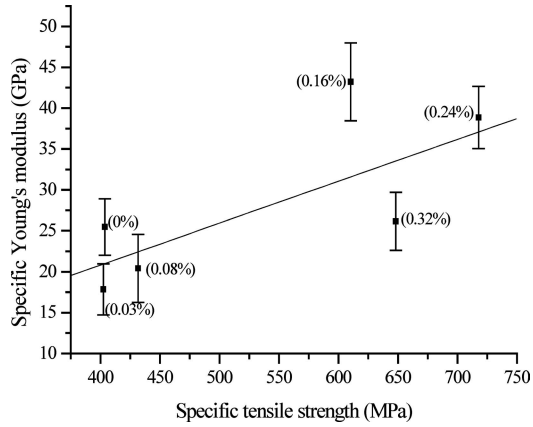


Figure 17 Specific modulus versus specific strength of hemp, sisal and jute fibre bundles following caustic soda treatment.

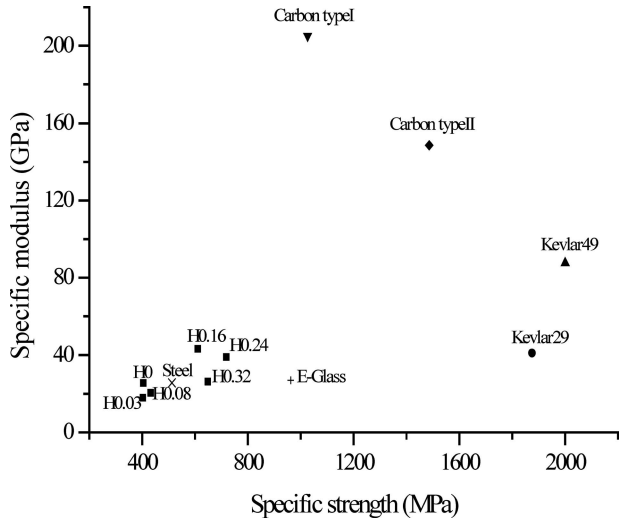


Figure 18 Specific modulus versus specific strength of 0.24% NaOH treated hemp fibre bundles and some man-made fibres (H0, H0.03, H0.08, H0.16, H0.24 and H0.32 represent untreated, 0.03%, 0.08%, 0.16%, 0.24% and 0.32% NaOH treated hemp fibre bundles).

crease in the specific tensile strength (Fig. 16). A higher value of the coefficient of correlation (R) (Fig. 17-inset) indicates less scatter of the values hence good control of experimental conditions.

3.4. Comparison between hemp and synthetic fibres

Table V [18] show the mechanical properties of hemp fibre bundles with selected synthetic fibres. To avoid duplication of results value for hemp fibre bundles are shown in Table IV and for comparison purposes only specific values have been used to plot Fig. 18.

The specific strength versus specific modulus is plotted for untreated and alkali treated hemp fibre bundles and high-performance fibres (Fig. 18) namely Kevlar 29, Kevlar 49 Carbon Type I, Carbon Type II, E-Glass and steel fibres. Untreated hemp fibre bundles exhibit approximately the same ratio of modulus to strength as that of steel and E-Glass fibres whereas hemp fibre bundles treated at 0.03% and 0.08% caustic soda concentration show inferior ratios to the rest of the fibres. However, hemp fibre bundles treated at 0.16% and 0.24% caustic soda concentrations exhibit about 69% and 52% respectively higher ratio of modulus to strength than steel. E-glass is less by 61% and 44% for the same concentrations of caustic soda (0.16% and 0.24%) treatment on hemp fibre bundles. Carbon type I exhibit the highest ratio of modulus to strength than the rest of the fibres followed by Carbon type II and Kevlar 49 fibres respectively. The good performance of alkalised hemp fibre bundles makes them particularly useful as reinforcement for composite manufacture.

However, the good performance of the synthetic fibres is mainly due to their well engineered structure such as linearity and very small diameter compared to plant fibre bundles, which possess a hollow non-linear molecular structure coupled with the presence of natural and processing defects along the fibre length. These results show that plant fibres can provide useful replacements for synthetic fibres as long as they are carefully handled to minimise structural damage and in some cases chemically modified to improve crystalline order.

3.5. Fracture surface topography of the fibre bundles

Hemp fibres have been found to consist of bundles of single ultimate cells as indicated in the SEM micrographs Figs 19–21 and also examined in this section. The fibres contain cell wall layers with the lumen space at the centre. The fracture mechanism of plant fibres bundles has been well documented by McLaughlin and Tait [2], Kulkarni *et al.* [10] and Morton and Hearle [6]. Some authors have reported the fracture mechanism of plant fibres when used as reinforcement for polymeric resins [19, 20]. In all these studies plant fibres show a fibrillar splitting and buckling. Dinwoodie [21] and Davies and Bruce [22] carried out a study on micro-compressions in wood and flax fibres respectively and found that damaged fibres had lower tensile strengths and moduli. Hughes [5] conducted a study on the micro-compression defects of hemp and flax fibres and found similar results. In this research the inherent (nodes) and processing defects in hemp fibre bundles are seen as the major sites for failure initiation in tensile loading. Figs 19–21 shows SEM micrographs of hemp fibre bundles fractured in tension.

The fracture mechanisms of an untreated hemp fibre bundle show brittle failure of the ultimate fibre cell wall and delaminating (Fig. 19a). The failure is not at the same stress level indicating the presence of cell wall defects along the fibre, which then develops stress intensities

TABLE V Physical and mechanical properties of high performance and other fibres

Fibre type	Tensible strength (MPa)	Specific tensile strength (MPa)	Young's modulus (GPa)	Specific young's mdulus (GPa)	Specific gravity
Kevlar 29	2700	1875	59	40.97	1.44
Kevlar 49	2900	2000	127	87.59	1.45
Carbon Type I	2000	1025.64	400	205.13	1.95
Carbon Type II	2600	1485.71	260	148.57	1.75
E Glass	2500	961.53	70	26.92	2.60
Steel	4000	512.82	200	25.64	7.80

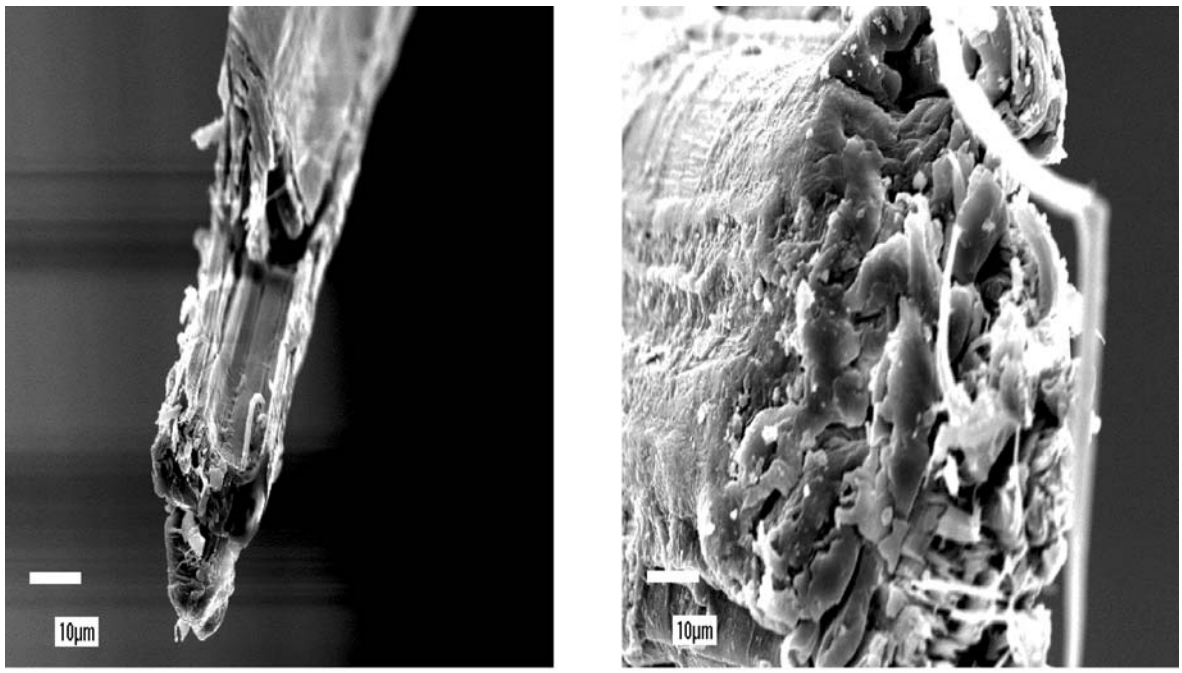


Figure 19 SEM micrographs of (a) untreated and (b) 0.03% NaOH treated hemp fibre bundles fractured in tension.

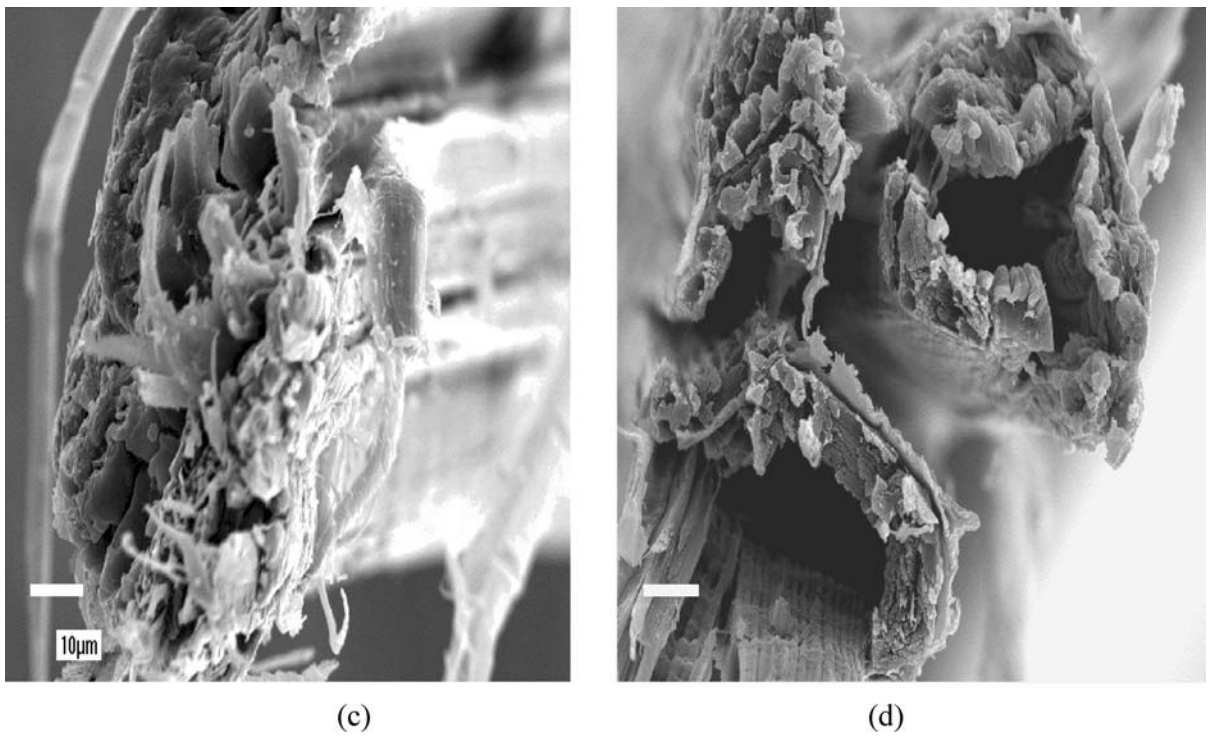
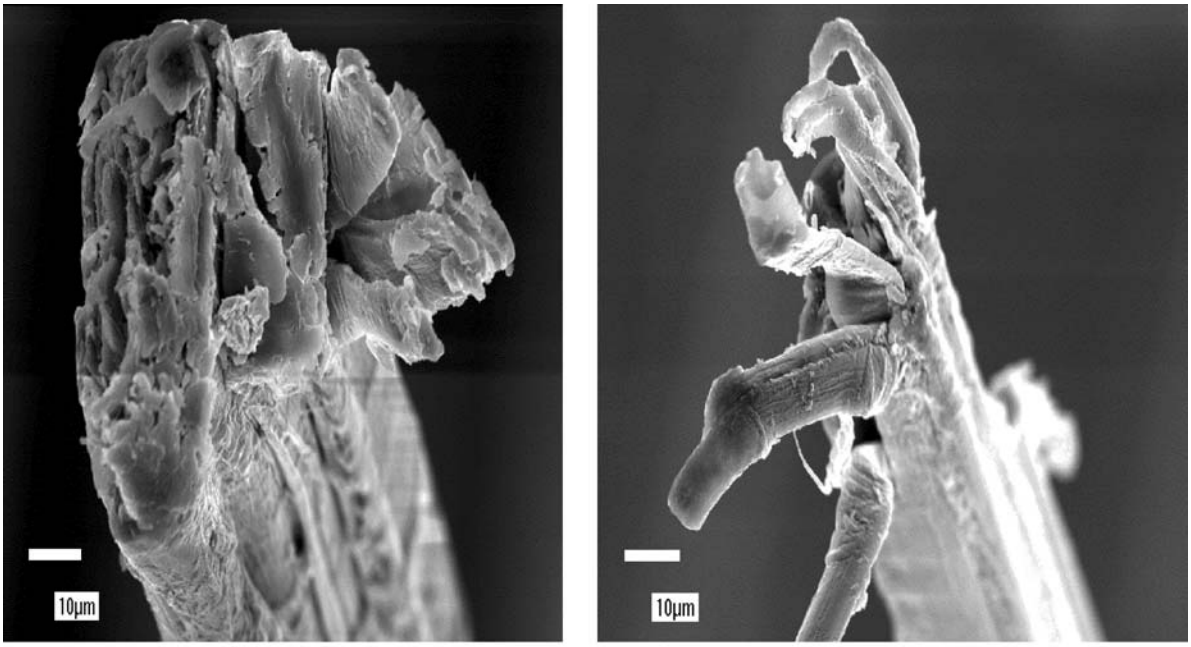


Figure 20 SEM micrographs of (c) 0.08% and (d) 0.16% NaOH treated hemp fibre bundles fractured in tension.

leading to failure. Alkalised hemp fibre bundles at different caustic soda concentrations show different failure profiles and the fracture in these cases occurs at the same stress level, which is an indication that most of the weak points have been eliminated and/or uniform distribution of crystallites is attained. This is expected because alkalisation in plant fibres swells the fibre cell wall allowing the rearrangement of the crystallites into a well-ordered state thus reducing the number of weak places. By reducing the weak places the stress is then evenly distributed along the fibre length. The buckling and unravelling of ultimate fibres seen in alkalised hemp fibre bundles, seen



(e) (f)

Figure 21 SEM micrographs of (e) 0.24% and (f) 0.32% NaOH treated hemp fibre bundles fractured in tension.

in Figs 19–21 are an indication of the uncoiling of the micro-fibrils. Morton and Hearle [6] and McLaughlin and Tait [10] have reported similar observations in cotton and bowstring hemp fibres respectively.

4. Conclusions

- There is a negative correlation between the tensile strength and Young's modulus of hemp fibre bundles
- Using caustic soda to alkalise the fibre bundles influences the mechanical properties of hemp and mechanical properties are controlled by the concentration of caustic soda, which modifies the fibre structure. The mechanical properties measured have been found to be dependent on amount of cellulose and the crystallinity index of individual hemp fibre bundles.
- The overall increase in tensile strength and Young's modulus of hemp fibre bundles with increase in the concentration of caustic soda, which is the reverse of the trend observed for mechanical properties versus cellulose content and crystallinity index implies that the crystallinity index is not a measure of the crystalline packing order.
- The slight increase in the cellulose content and crystallinity index of hemp fibre bundles following alkalisation indicates a highly compacted crystalline structure with very little amount of amorphous materials. A major influence of caustic soda is the bulking of the cell wall and improved parking order and increased amorphous materials. The resistance of the crystalline regions to bulk following alkalisation is characteristic of inherently high ordered crystallite cellulose such as in hemp fibres compared to those with less ordered crystalline cellulose such as in sisal and jute fibres reported in Part II and Part III of this series of publication.
- A key aspect of this work has been the development of new, quicker and easier techniques for determining the elastic moduli of the micro-fibrils using the cellulose content and crystallinity index. The micro-fibril angle has also been determined.
- The inferior performance of plant fibre to the high-performance fibres is attributed to their high micro-fibril angle, crystalline linearity and their large diameters compared to the linear structures and small diameter of synthetic fibres. The presence of lumens in plant fibres also contributes to their lower mechanical properties.
- Alkalisation has been found to increase the specific mechanical properties of hemp fibre bundles thus enabling it to compete with synthetic high-performance fibres up to a limit.
- Hemp fibre bundles possess good mechanical properties, which imply that they can successfully be applied as reinforcement for polymeric materials.

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