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NATURAL COMPOSITES: STRENGTH, PACKING ABILITY AND MOISTURE SORPTION OF CELLULOSE FIBRES, AND THE RELATED PERFORMANCE OF COMPOSITES

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ABSTRACT

Biobased materials are becoming of increasing interest as potential structural materials for the future. A useful concept in this context is the fibre reinforcement of materials by stiff and strong fibres. The bio-resources can contribute with cellulose fibres and (bio) polymers from hemicelluloses. This offers the potential for stiff and strong biocomposite materials, but these have some limitations and obstacles to full performance. The focus will be on the structure, strength and stiffness of cellulose fibres, on the (unavoidable) defects causing large reductions in strength and moderate reductions in stiffness, on the packing ability of cellulose fibres and the related maximum fibre volume fraction in composites, on the moisture sorption of cellulose fibres and the related mass increase and (large) hygral strains induced, and on the mechanical performance of composites.
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Keywords: Cellulose fibres, Structure, Strength, Stiffness, Defects, Fibre packing ability, Moisture sorption, Composite performance

1. INTRODUCTION

Biobased materials are becoming of increasing interest as potential structural materials for the future. A useful concept in this context is the fibre reinforcement of materials by stiff and strong fibres. The bio-resources can contribute with cellulose fibres and (bio) polymers from hemicelluloses. This offers the potential for stiff and strong biocomposite materials, but these have some limitations and obstacles to full performance. The focus will be on the structure and strength of cellulose fibres and the mechanical performance of composites.

The cellulose fibres have potentially (very) high strength and stiffness. In general, the fibres contain **defects**, even in the as-grown condition. The defects are typically disorder in the otherwise crystalline structure. It is expected that the (potential) effects of defects, on e.g. stiffness and strength, will be governed by the volume content of defects.

For these composites, the aim is to use high fibre content, good fibre alignment and ensure low porosity in the composite. To achieve high fibre volume fraction in a composite, a good **packing ability** is needed. If very high fibre contents are aimed at, the correspondingly very low matrix content will lead to the presence of structural (unavoidable) porosity in the final composite. This situation defines a **maximum fibre volume fraction**, at which the volume of matrix is just sufficient to avoid structural porosity.

In the case of synthetic fibre composites, the **moisture sorption** behaviour is well documented. In these traditional composites, moisture sorption is dominated by the isotropic matrix with higher moisture sorption capacity and lower tensile stiffness than the reinforcing fibres. In contrast, moisture sorption in cellulose fibre composites is dominated by the anisotropic fibres with (much) higher moisture sorption capacity and higher tensile stiffness than the matrix. Due to these fundamental differences, the existing knowledge of how to analyse and calculate moisture expansion in composites needs to be re-evaluated for the case of natural composites.

2. CELLULOSE FIBRES AND COMPOSITES

2.1 Structure and strength of cellulose fibres

The cellulose is chemically based on the polysaccharide $(C_6H_{10}O_5)_n$, with molecular weight of 162. Practical cellulose fibres have typically 60-70% cellulose, the rest being hemicelluloses and lignin, [1]. Basically the cellulose has a crystalline structure (monoclinic) with unit cell dimensions of about 1 nm x 0.8 nm x 0.8 nm. In fibres the cellulose is partly crystalline and partly amorphous. The crystallinity for cellulose fibres derived from flax and hemp plants are typically about 90%, [2].The theoretical properties for fully crystalline, pure cellulose can be calculated from the crystal structure and potential energy models for the bonding between the atoms. The theoretical maximum values are: density 1.64 g/cm^3, stiffness 120 GPa, strength 15,000 MPa, see Fig.1.

The practical, experimentally derived values for cellulose fibres from e.g. flax and hemp plants, are density 1.5 g/cm^3, stiffness 50-70 GPa, strength 600-900 MPa. For stiffness practical values are rather close to the theoretical value, so some potential still exists for improvement, for strength the practical values are significantly lower than the theoretical values and thus a large potential exists for improvement, but this is met with some obstacles, as described in the following sections.

Cellulose – the structural component in plant fibres

Cellulose microfibril consisting of aligned cellulose chains
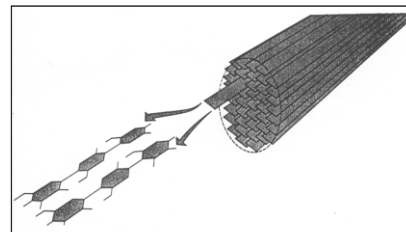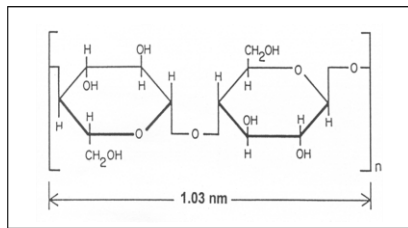
Properties of crystalline cellulose (theoretical)

**Density: 1.64 g/cm³;   Stiffness: 120 GPa;   Strength: 15,000 MPa**

Fig 1   Cellulose structure and properties.

2.2 Defects in cellulose fibres

The cellulose fibres, in general, contain defects, even in the as-grown condition. This initial defect type and content has not been established. The defects are typically disorder in the otherwise crystalline structure, and they are called kink

bands or dislocations. The defects are normally observed by (optical) microscopy and quantified by the number density of defects. It is expected that the (potential) effects of defects, on e.g. stiffness and strength, will be governed by the volume content of defects, and related studies are in progress. It is expected and observed, qualitatively, that processing of fibres, when converting plants to yarns, will have a damaging / defect generating effect on the fibres, see Fig.2.

A study has been made [3], where it is assumed that each processing step has a similar effect in generating defects in the fibres. A range of flax and hemp fibres have been given processing steps from zero to 5. The chemical composition remained in practice unchanged at about 70% cellulose, and the crystallinity of cellulose remained unchanged at the level of 90-95%. The fibre bundle (yarn) strengths have been measured, and the strength values decrease monotonically, see Fig.3, with an exponential decay, giving a strength decrease of about 25% per processing step. The processing from plant to yarn is an unavoidable chain of process steps to obtain useful fibres (preforms) for composites, so this chain of processes is an obstacle to high strength. The potential action will be to reduce the number of steps and attempt to make individual steps as mild as possible in terms of defect generation. The potential processing types include chemical, biological and mechanical treatments.
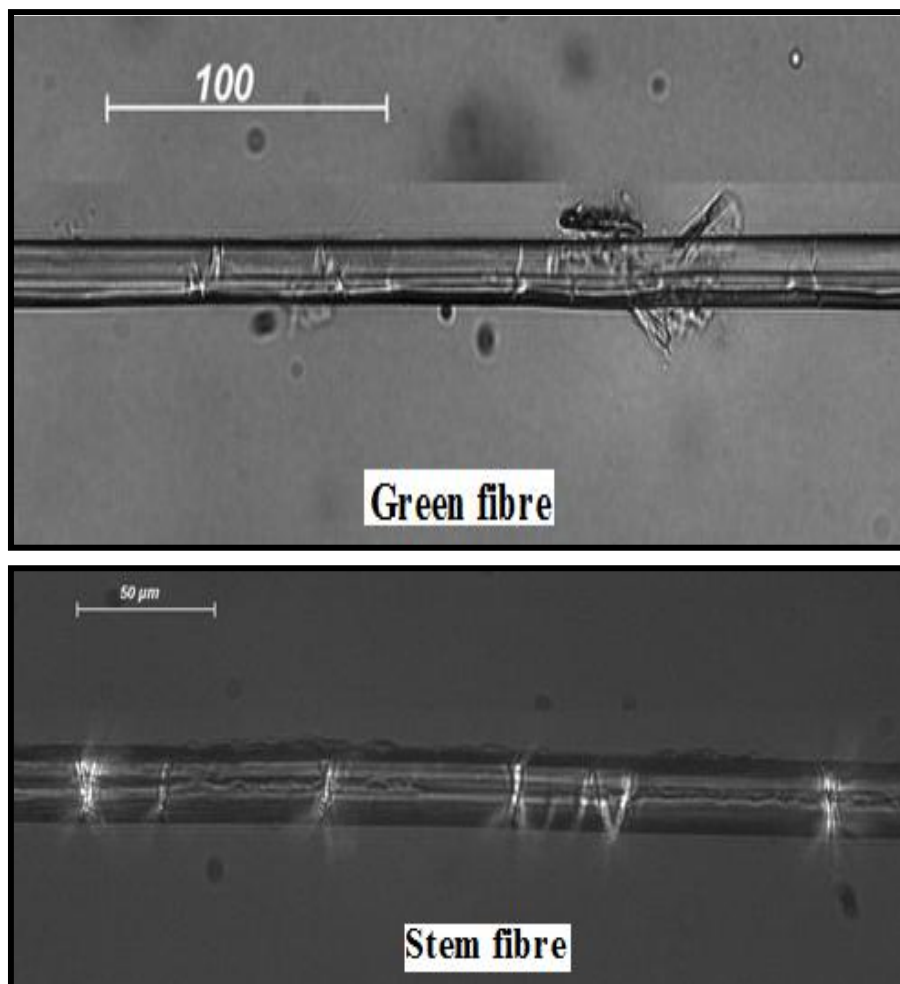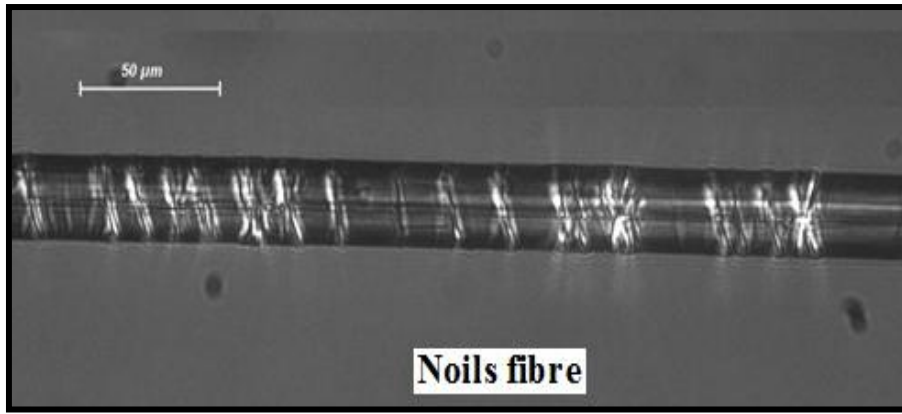
Fig 2   Defects in flax cellulose fibres, caused by processing. The Green fibres (top picture) have formally no processing (N = 0), the Stem fibres (middle picture) have been processed through 1 step, retting (N = 1), and the Noils fibres (bottom picture) have been processed through two steps, retting + scutching (N = 2).

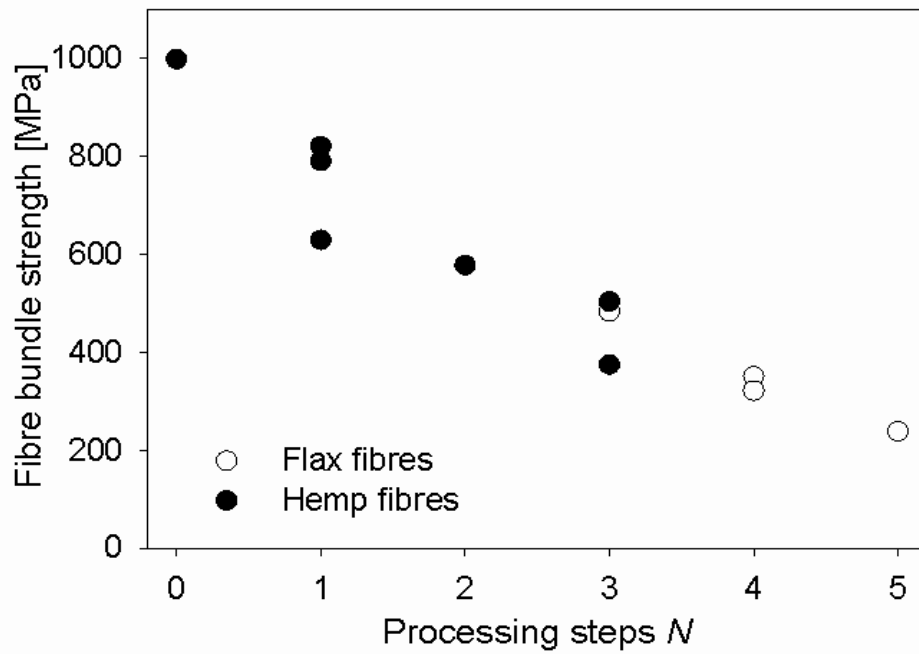

Fig 3   Fibre bundle strength for flax fibres and hemp fibres, after a series of processing steps, from zero to five steps.

2.3 Packing ability and maximum fibre fraction

Composites made from cellulose fibres must follow the same rules as other composites in order to achieve good mechanical properties. Therefore, the aim is to use high fibre content, good fibre alignment and ensure low porosity in the composite. The cellulose fibres present some difficulties in this respect, caused by their non-circular cross section, their non constant cross sectional area and their branching of individual fibre elements. This is in contrast to e.g. glass fibres which have circular, constant cross section and have straightness. To achieve high fibre volume fraction in a composite, a good packing ability is needed, experiments (Fig 4) show that glass fibres in unidirectional configuration can be packed to about 70 %, while cellulose fibres in unidirectional configuration can be packed to 55-60%. For random fibre orientation configurations the values are 55% and 40-45%, respectively. If higher fibre contents are aimed at by lowering the matrix content, this correspondingly lower matrix content will not be enough to fill the space between the maximally packed fibres, and this will lead to the presence of structural (unavoidable) porosity in the final composite, [4]. This porosity is over and above any porosity in the matrix, caused by e.g. the processing of the composite. This situation defines a **maximum fibre volume fraction**, at which the matrix content is just sufficient to avoid structural porosity, see Fig. 5. This maximum fibre volume fraction corresponds to a transition fibre **weight** fraction, beyond which structural porosity develops.   A model has been established [4,5] for the effect of fibre content and porosity content on the density and stiffness of the resulting composite, see section 2.5 Composite performance.
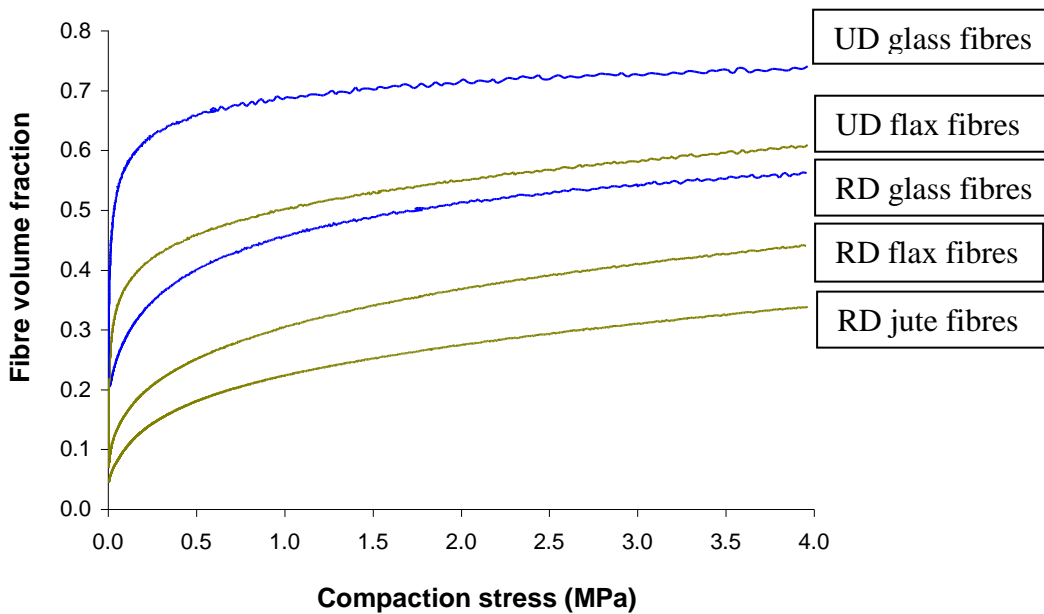

Fig 4   Packing ability of fibres as a function of compacting pressure, fibres are glass, flax and jute, UD is unidirectional fibre arrangement, RD is random directional fibre arrangement,
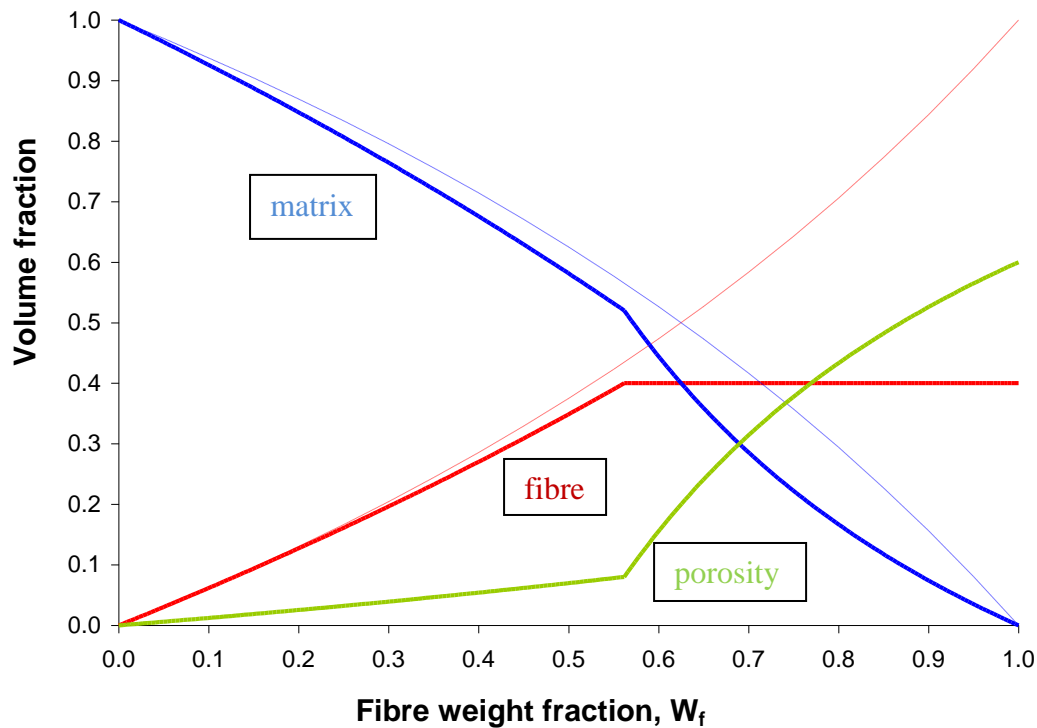
Fig 5   Volumetric composition for composites, with fibre density larger than matrix density (cellulose density 1.5 g/cm^3, matrix density 1.1 g/cm^3), limited packing ability of fibres, and structural porosity. The volume fractions for fibres (red curve), for matrix (blue curve) and for porosity (green curve) are plotted versus weight fraction of fibres. At the (transition) fibre weight fraction of ca 0.57 the packing of fibres is maximum, and the fibre volume fraction stays constant for higher fibre weight fractions, this causes the (structural) porosity to develop and increase.

2.4 Moisture sorption of cellulose fibres and their composites

In the case of synthetic fibre composites, e.g. glass fibre composites, the relationship between moisture content and dimensional changes is well documented (e.g. see review in [6]). The moisture properties of these traditional composites are dominated by the isotropic matrix with higher moisture sorption capacity and lower tensile stiffness than the fibres. In contrast, the moisture properties of plant fibre composites are dominated by the anisotropic fibres with (much) higher moisture sorption capacity and higher tensile stiffness than the matrix. Thus, due to these fundamental differences, the existing knowledge of how to analyze and predict the moisture content and the dimensional changes of composites need to be further evaluated for the case of plant fibre composites, [7]. Aligned hemp yarn/thermoplastic matrix composites with four different fibre contents were exposed to five levels of ambient humidity and their equilibrium weights and dimensions were measured resulting in a comprehensive set of experimental data. The results were analyzed with moisture-related micromechanical models where the measured properties of the constituent fibre and matrix phases, and the composition of the composites are used to predict the properties of the composites.

The moisture absorbed by a material causes an increase of the total mass of the water-containing material, and an increase of the total dimensions, i.e. linear dimensions and volume, of the water-containing material. The mass (weight) increase is normally represented by the **moisture content** which is defined as the relative mass increase. The dimensional changes (normally an increase of dimensions) are represented by the **hygral strains** for the (three) linear dimensions and for the volume of the material. These two parameters are governed by and related to the moisture of the environment, normally called the relative humidity (RH). This behavior is of interest for any individual (monolithic) material, e.g. fibres and matrices, respectively. For composites composed of fibres and matrix, e.g. cellulose fibres in a polymer matrix, it is also of importance to elaborate the composite performance as related to the behavior of its components. This performance is governed by the (dominating) parameter fibre fraction of the composite. For the **mass** based moisture content the fibre **weight** fraction is a useful parameter, while for the **volume** based hygral strains the fibre **volume** fraction is most convenient in establishing (simple) relationships for the moisture effects in composites.

The models for the relations between moisture content and humidity (RH) and between dimensional strains and humidity (RH) are described by an empirical equation which simulates the S-shaped relation between the moisture content and hygral strains, respectively, and the RH. The simple geometrical models and the stress equilibrium for composites are used to derive relations for moisture effects in composites, based on the fibre weight and volume fractions, [7].

A set of comprehensive experiments have been made for hemp fibres in PET polymer matrix, both for the fibres themselves and for the related composites, [7]. For practical reasons, the moisture contents are referred to 65% RH. The results are used to extract the basic moisture related properties for cellulose fibres, PET polymer, and for the related composites.

The composite moisture content versus the fibre weight fraction is shown in Fig 6, and the composite dimensional strains are shown for strain in the fibre direction in Fig 7 and for strains in the transverse directions in Fig 8, versus fibre volume fraction. The derived values of moisture content and dimensional strains for the cellulose fibres and for the PET matrix , respectively, are plotted versus the relative humidity (RH), and these curves are used to extract values, related to "dry material", for the moisture parameters at 100%RH for cellulose fibres and for PET polymer. The table 1 gives these parameters, related to "dry material".
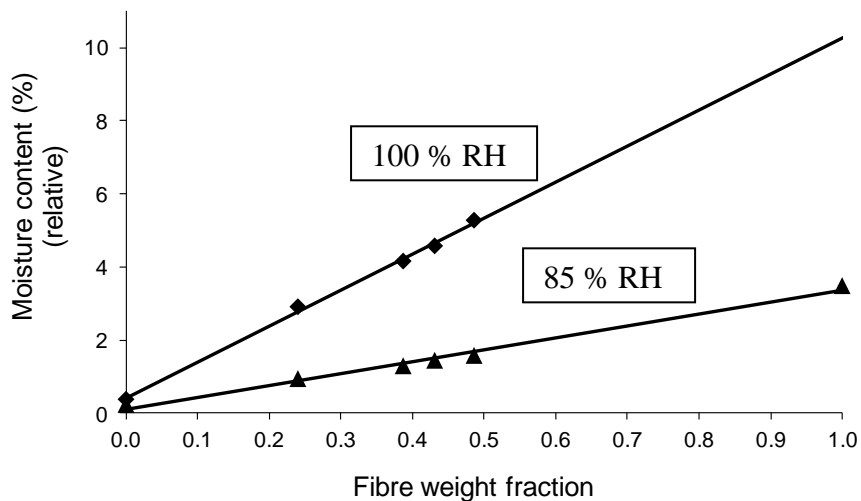

Fig 6   Relative moisture content of composites as a function of fibre weight fraction. Results are shown for composites conditioned at different humidity levels.
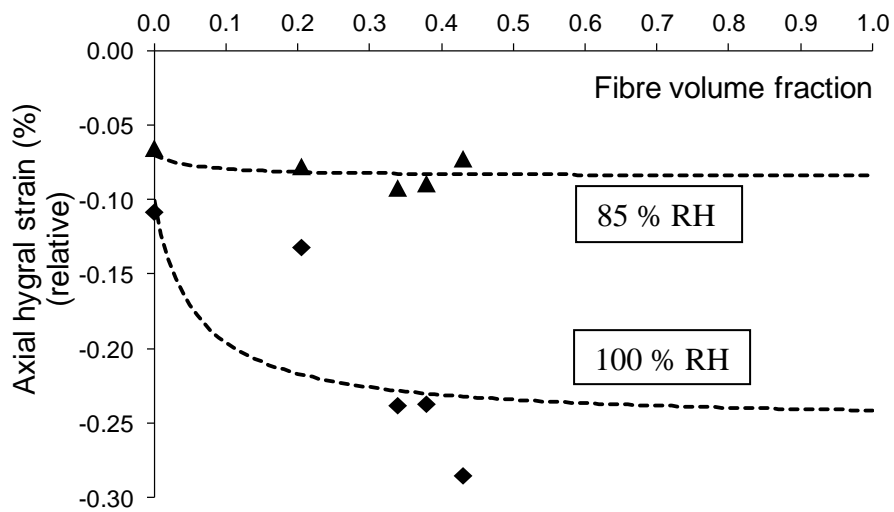
Fig 7   Hygral strain of composites as a function of fibre volume fraction, at different humidity levels: axial strain in the fibre direction,
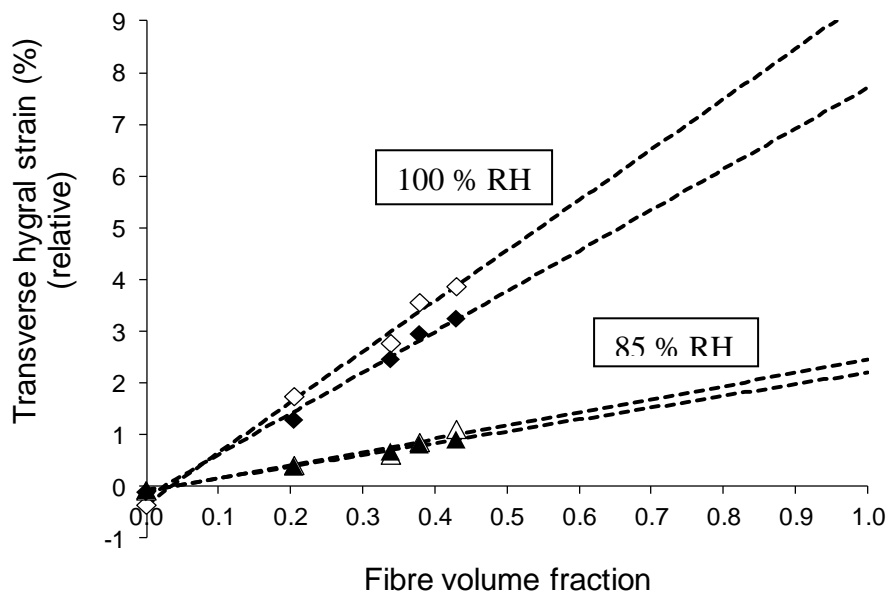

Fig 8   Hygral strain of composites as a function of fibre volume fraction, at different humidity levels: transverse strains in the width direction (filled symbols) and in the thickness direction (open symbols).

Table 1

Moisture content Hygral strains	Cellulose fibres	PET polymer
Moisture content, M	+ 0.1850	+ 0.0130
Axial strain, e (x)	- 0.0028	+ 0.0110
Transverse strain, e (y)	+ 0.1220	+ 0.0110
Transverse strain, e (z)	+ 0.1390	+ 0.0110
Volumetric strain, e (vol)	+ 0.2586	+ 0.0330

It can be noted that the axial strain for the cellulose fibre is small and negative, this is equivalent to the behavior for thermal expansion, while the hygral strains are large in transverse directions.

These values can then be used to calculate the moisture performance of any composite, composed of these (hemp) cellulose fibres and PET polymer matrix. As examples, the situation for **moisture content** versus RH is shown for fibre, matrix and composite (at fibre weight fraction 50%) in Fig 9, and versus fibre weight content for composites at (three) selected RH values, in Fig 10.   The **hygral strains** are dominated by the fibres, and thus the strain in the fibre direction is practically zero, while strains in transverse directions are fairly large, and these dominate the volumetric strain,
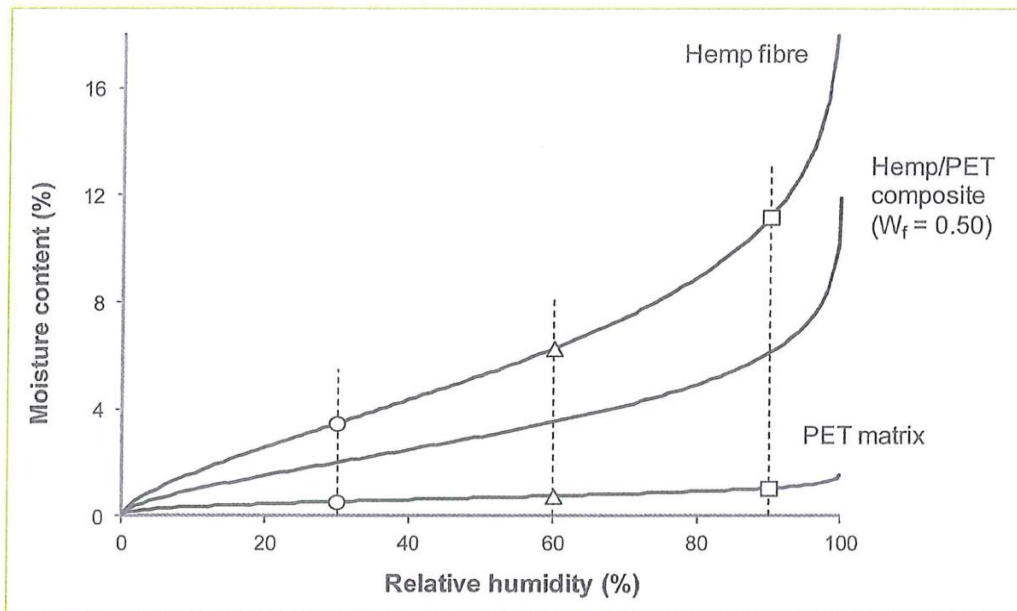(e (vol) = e(x) + e(y) + e(z)) .

Fig 9   Moisture contents of hemp fibres, PET polymer and hemp/PET composites (fibre weight fraction 50 %), as a function of relative humidity
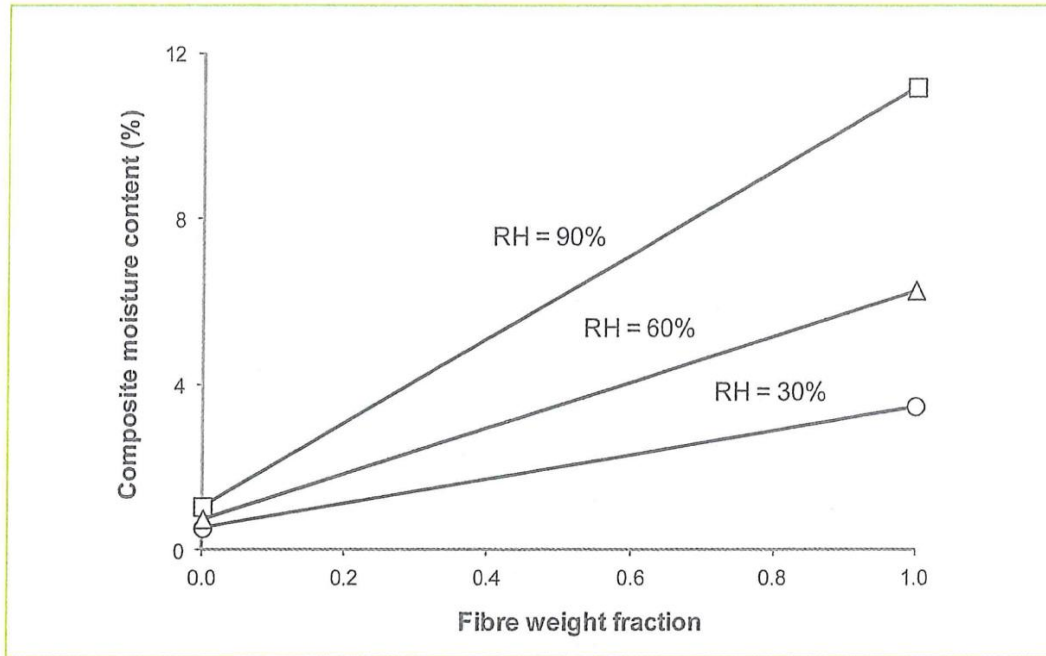
Fig 10 Composite moisture content of cellulose fibre / PET polymer composites, as a function of fibre weight fraction, at three humidity levels as marked in Fig 9. At weight fraction 0.0 the three markings indicate the corresponding points on the matrix curve of Fig 9, at weight fraction 1.0 the three markings indicate the corresponding points on the fibre curve of Fig 9

2.5 Composite performance

A model has been established for the effect of fibre content and porosity content on the density and stiffness of the resulting composite, [4, 5]. This shows maximum values for density and stiffness at the transition fibre weight fraction, thus indicating an optimal combination of fibre content and porosity content, see Fig.11. This model elucidates the potential for cellulose fibre composites in terms of stiffness (and strength), but also defines the limit to stiffness and strength. The obstacles are the moderate packing capability of the cellulose fibres, and improvements should be focused on improving the uniformity of morphology of cellulose fibres.
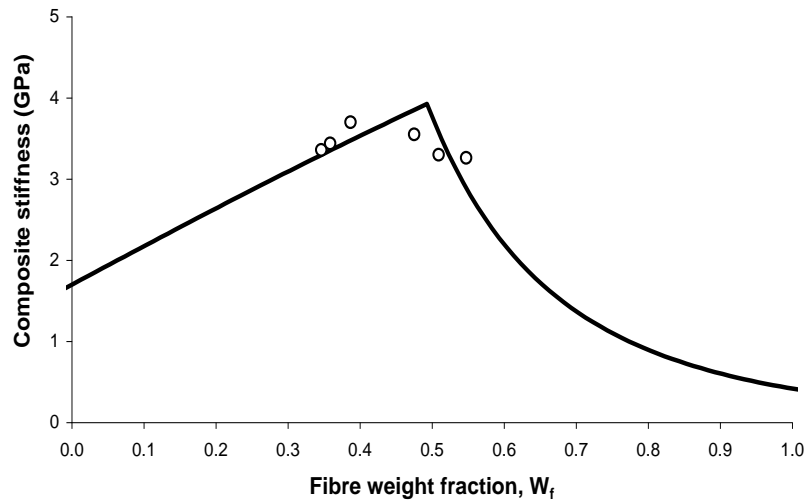
Fig 11 Composite stiffness for jute fibre / polypropylene composites with 2-D random fibre orientation distribution. Fibre density is 1.52 g/cm^3, matrix density 0.91 g/cm^3, transition fibre **weight** fraction is 0.49, corresponding to maximum fibre **volume** fraction of 0.34, the maximum composite stiffness is obtained at this fibre fraction. Stiffness is plotted versus fibre weight fraction (calculated curve), and the experimental data are shown as circular points

3. CONCLUSIONS

The present situation for cellulose fibres is for   stiffness: theoretical value 120 GPa, practical value 60-80 GPa,   for strength: theoretical 15,000 MPa, practical value 600-900 MPa,   cellulose crystallinity about 90%. The processing induced defects reduce fibre (bundle) strength by about 25% per processing step. Packing ability of cellulose fibres (unidirectional) is 55-60%. Maximum composite properties are   obtained at a limiting fibre volume fraction, in combination with no structural porosity. The moisture sorption and (equilibrium) content of cellulose fibres is higher than that of typical polymer matrices, leading to high mass increase and to hygral strains, which are close to zero in the axial direction and large in transverse directions. The future approach should be aimed at (i) fibres with higher cellulose content and higher crystallinity, (ii) improved processing of cellulose fibres causing reduced defect content, (iii) developing cellulose fibres with uniform morphology in order to give better packing of fibres and thus higher maximum fibre volume fraction in composites, (iv) the potential use of nano scale crystalline cellulose fibrils leading to very high inherent stiffness and strength of fibres, (v) reduction of the moisture sorption by chemical modification of cellulose, in the bulk and / or at the surface of the cellulose fibres.

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