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LETTER

A fibre diameter distribution factor (FDDF) for natural fibre composites

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Introduction

In its generalised form, the rule-of-mixtures (ROM) for the tensile modulus of a fibre-reinforced composite is:

$$E_c = \eta_l \eta_o V_f E_f + V_m E_m \quad (1)$$

where η_l is the fibre length distribution factor (FLDF) and η_o is the fibre orientation distribution factor (FODF). The FLDF ranges between 0 (fibres below the critical length) and 1 (continuous fibres). The FODF ranges between 0 (fibres aligned transverse to the stress) and 1 (fibres aligned with the stress). V_f and V_m are the volume fractions of the fibre and matrix, respectively. E_f and E_m are the elastic moduli of the fibre and matrix, respectively. It is normally assumed that the fibres are uniform, parallel, continuous and may be anisotropic, that the matrix is homogeneous, and that there is perfect bonding between the fibres and matrix.

The ROM equation has proved adequate for the estimation of the properties of man-made fibre-reinforced composites. However, there is now increasing interest in the use of natural fibres as reinforcements [1–8]. These fibres are generally accepted to have much greater variation in their cross-sectional area (both in being of non-circular cross section and in the effective "diameter"). Virk et al. [9] have shown that the Young's modulus of jute fibres in tension is sensibly independent of fibre length. In contrast, Young's modulus tends to decrease (approximately linearly) with increasing fibre "diameter" (Fig. 1). Note that the R^2 values in the Figure indicate that a natural logarithmic fit is a more probable model than a linear fit. Similar reductions in fibre modulus with increasing fibre diameter have been reported by Bodros and Baley [10] and Lamy and Baley [11] for flax and nettle fibres, respectively.

The proposed fibre diameter distribution factor

The data can be reduced to the following linear (Eq. 2) and natural logarithmic (Eq. 3) forms for fibre modulus:

$$E_f = E_{f_0} - md \quad (2)$$

$$E_f = E_{f_0} - m \ln(d) \quad (3)$$

where E_{f_0} is the fibre modulus obtained by back-extrapolation of the line to a notional fibre diameter of zero, m is the (negative) slope of the line, and d is the fibre diameter.[1] The respective values are given in Table 1.

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[1] Consequent upon the material presented above, we can substitute the data for jute fibres from Fig. 1 into the natural logarithm model (Eq. 3) to give Eq. 9:

$$E_f = 98.88 - 17.28 \ln(d) \quad (9)$$

The modulus of jute fibre at zero diameter is 98.88 GPa when measured assuming the "apparent" diameter for a circular cross section. Using the fibre area correction factor of 1.42 for this batch of jute fibres [33], we can correct this modulus to account for the non-circular cross section (98.88 × 1.42) and derive an elastic modulus of 140 GPa. A value of 140 GPa was estimated for cellulose when using X-ray diffraction to determine the strain [23]. Upper values for the modulus of cellulose I crystals are reported to be in the range 137–143 GPa [14–17, 36–38].

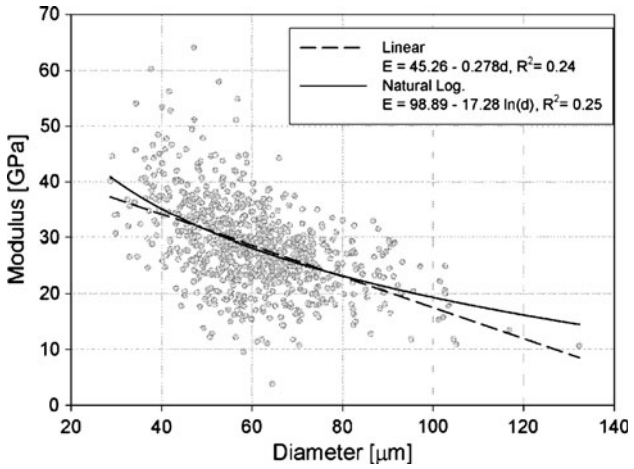

Fig. 1 Variation of the Young's modulus of jute fibres with fibre diameter

The authors [8] have previously proposed that the ROM should be modified (Eq. 4) to include an additional term to account for the dependence of the modulus of natural fibres on their cross-sectional area, to be known as the fibre "diameter" distribution factor (FDDF), η_d:

$$E_c = \eta_d \eta_l \eta_o V_f E_{f_o} + V_m E_m \tag{4}$$

We acknowledge that natural fibres are not normally of circular cross section but the natural fibre industry is now so ingrained with that false parameter that we retain that terminology in this article. The mean fibre modulus can be obtained empirically from the linear or natural logarithmic form of Eq. 5:

$$\begin{aligned} \frac{\sum_{i=1}^{n} E_{f_i}}{n} &= E_{f_m} = E_{f_0} - m d_m \\ \frac{\sum_{i=1}^{n} E_{f_i}}{n} &= E_{f_m} = E_{f_0} - m \ln(d_m) \end{aligned} \tag{5}$$

where E_{f_m} is mean fibre modulus, d_m is mean fibre diameter for a batch, so that η_d can be determined from Eq. 6 (linear model) or Eq. 7 (natural logarithmic model):

$$\eta_d = \frac{E_{f_m}}{E_{f_0}} = \frac{E_{f_0} - m d_m}{E_{f_0}} = 1 - \frac{m d_m}{E_{f_0}} \tag{6}$$

$$\eta_d = \frac{E_{f_m}}{E_{f_0}} = \frac{E_{f_0} - m d_m}{E_{f_0}} = 1 - \frac{m \ln(d_m)}{E_{f_0}} \tag{7}$$

Using the data set in reference [9], this new expression enables the mean modulus of a different sample to be calculated assuming E_{f_0} and m are sample independent (i.e. a material characteristic). Predicted and measured mean modulus values for the jute fibres are shown in Table 2. The predictions are based on the E_{f_0} and m values calculated from 785 samples. The measured values for the 10 mm fibres in the data set analysed are consistently at the lower end of the range of values for all fibres with the consequent high error shown for this group.

Prediction of the FDDF

It would be useful, in the context of the prediction of the mechanical properties of natural fibre composites, to develop a more rigorous theoretical basis for the FDDF considering the theoretical limit for the modulus of a 100% cellulose crystal, the degree of crystallinity in the cellulose fibres and the orientation of the structural elements relative to the fibre principal axis.

Kroon-Battenburg et al. [12] calculated a modulus for the cellulose crystal of 136 ± 6 GPa while Tashiro and Kobayashi [13] obtained a value of 167.5 GPa for type I native cellulose when thermal motion of the chain was "frozen." Šturcová et al. [14] used a molecular mechanics computer simulation and an empirical force field to predict the modulus of a highly oriented chain of cellulose to be 145 GPa. Tanaka and Tadahisa [15] used molecular simulation to estimate the Young's modulus for the cellulose I_β crystal (type B packing typical of plants) at values in the range 89–172 (1 × 1 × 10 unit cells) or 124–171 GPa (4 × 4 × 10 unit cells).

Sakurada et al. [16] used X-ray diffraction to measure cellulose I crystal deformation in bleached ramie fibres and obtained a Young's modulus of 137 GPa. Nishino et al. [17] have reported a measured value of 138 GPa, while Šturcová et al. [14] used a Raman spectroscopic technique (the 1095 cm^{-1} band has an initial linear strain sensitivity of -2.4 ± 0.2 cm^{-1}/%) to measure the elastic modulus of tunicin whiskers (95% crystalline cellulosic material produced by a marine animal) as ~143 GPa.

However, natural fibres are neither 100% cellulose nor wholly crystalline and hence the value for E_{f_0} should normally be lower than that for highly oriented molecules. As a first approximation, it can be assumed that amorphous cellulose, hemicellulose, lignin and the pectin binder (the

Table 1 Data for the linear equation (Eq. 2) from several authors

Fibre	No. of fibres	E_{f_0} (GPa)	m (GPa/μm)	m/E_0 (%/μm)	Reference
Nettle	90	150.56	3.2991	2.2	Bodros and Baley [10]
Flax	77	86.028	1.3781	1.6	Lamy and Baley [11]
Jute	785	45.276	0.2781	0.61	Virk et al. [9]

Table 2 Predicted and measured mean modulus for jute fibres

Fibre length (mm)	Mean diameter (μm)	Measured modulus (GPa)	Linear		Natural logarithm	
			Predicted modulus (GPa)	Error (%)	Predicted modulus (GPa)	Error (%)
6	53.89	32.50	30.29	−7.29	30.01	−8.31
10	57.67	26.30	29.24	10.06	28.84	8.79
20	61.06	31.00	28.30	−9.54	27.85	−11.32
30	59.59	31.00	28.71	−7.98	28.27	−9.66
50	61.53	28.30	28.17	−0.46	27.72	−2.11
100	64.34	27.10	27.39	1.05	26.94	−0.58
150	61.07	25.80	28.30	8.82	27.85	7.35
200	64.59	27.60	27.32	−1.03	26.88	−2.69
250	62.67	23.40	27.85	15.99	27.40	14.59
300	61.23	26.40	28.25	6.56	27.80	5.04

Table 3 Typical properties of the component materials in plant fibres

Material	Young's modulus (GPa)	Source	Reference
Amorphous cellulose	8.45	Experiment	Mark [18]
Amorphous cellulose	10.42 ± 1.08	Constant strain minimisation model	Chen et al. [19]
Dry hemicellulose	8.0	Indentation	Cousins [20]
Lignin at 3.6% moisture	6.7		Cousins [21]
Pectin hydrogels	~0.001–0.010	Fischer scientific P2	Liu et al. [34]
Pectin fibrils	0.003–0.114	Commercial citrus pectin	Lampitt et al. [35]

principal components of bast fibres) make a small contribution to the overall Young's modulus of the aligned cellulose fibre (Table 3). A more complex issue is that the molecules in the microfibrils (<10 nm diameter), the fibrils in the elementary fibres (10–25 μm diameter) and the elementary fibres in the technical fibres (50–100 μm diameter) are not necessarily aligned with the principal axis of the respective component.

Ruys et al. [22] have described the plant bast as composed of an inner soft woody core surrounded by bundles of long hollow fibres and an outer protective skin (epidermis) bound together by pectin and lignin. The fibre bundles consist of hollow, elongated thick-walled cells usually referred to as elementary fibres (of 25 μm diameter and 10–50 mm length in flax, or similar diameters but up to 150 mm long for hemp or ramie). Maturing elementary fibres develop a central hollow void (the lumen, being 2–5% of the cross-sectional area) surrounded by alternating walls of helically wrapped cellulose microfibrils in a matrix of amorphous hemicellulose. The middle secondary wall (the S2 layer) can comprise over 80% of the cross section and dominates the mechanical properties of the fibre. Vincent [23] for wood and Sanadi et al. [24] for sun hemp fibres have suggested that the elementary fibres have a structure similar to that shown in Fig. 2.

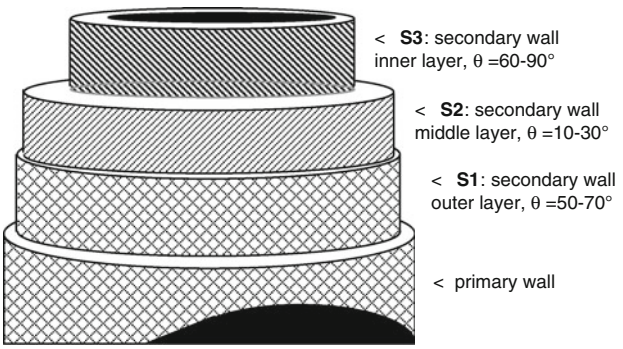

Fig. 2 Schematic representation of the structure of an elementary fibre (after Vincent [23] and Sanadi et al. [24])

Morvan et al. [25] have used TEM to show the presence of concentric layers around the lumen. Charlet et al. [26] used focussed ion beam milling to determine that the thickness of those layers was larger than previously believed (albeit that no quantitative analysis is reported). Those elementary fibres will have an orientation close to the hoop direction, and given the $\cos^4\theta$ dependence on orientation [27] with θ approaching 90°, they will thus make a relatively small contribution to the fibre modulus.

As the plant grows and ages, the fibre should increase in length and diameter, so:

- as the plant ages, lignification will decrease the proportion of crystalline cellulose in the fibre, α.
- as the fibre diameter increases, the orientation of the structural elements relative to the fibre principal axis, φ, will change and may align more closely with the hoop direction (by analogy with braids) or align closer to the principal axis [28], and
- as the fibre increases in size, we might expect an increase in the volume of the hollow core (lumen) as a proportion of the fibre volume, λ. Tamolong et al. [29] suggested that appropriate morphometric measurements might include a Flexibility Ratio (FR = 100 × lumen width of fibre/diameter of fibre) or a Runkel Ratio (RR = 2 × wall thickness/lumen width). However, we have been unable to identify such data for the ageing of jute fibres.

As a consequence of the above, a theoretical fibre "diameter" distribution factor, η_d, might take the form of Eq. 8:

$$\eta_d = \frac{(\alpha E_x - (1-\alpha)E_a)}{E_x} \sum_{i=0^\circ}^{180^\circ} \beta_i \cos^4 \phi_i (1-\lambda) \qquad (8)$$

where E_x is the modulus of crystalline cellulose, E_a is the modulus of amorphous organic materials and β is the proportion of each structural component at an angle to the fibre principal axis for each structural level. Note that the central term in the equation is equivalent to the Krenchel [27] equation for the FODF. Data for this equation can now be derived for jute fibre:

- $\alpha = \sim 0.62$ [30]
- $E_x = \sim 140$ GPa (from the experimental values cited from the literature above),
- $E_a = \sim 8.4$ GPa (unweighted average of the data, excluding the negligible proportion of pectins, in Table 3),
- Preston [31] has suggested that the angle between the cellulose molecules and the microfibril cell length in jute fibres can be up to 23° (so $\cos^4\varphi = 0.72$),
- the angle of the microfibrils to the principal axis of the elementary fibres is 8°, $\therefore \cos^4\varphi = 0.96$) [32],
- the angle of the elementary fibres within the technical fibres is taken as 1 pending identification of data (so we expect an over estimate of FDDF and moduli calculated using that parameter),
- the proportion of lumen in a fibre is of the order of 0.05 [22].

Using the data above gives an FDDF of 0.46 (0.638 × 0.72 × 0.96 × 1 × 0.95), so the predicted modulus of jute fibres would be 58.7 GPa (i.e. $\eta_d E_x$). Young's moduli for jute technical fibres are normally reported to be ~30 GPa (Table 2), although Virk has identified a "fibre area correction factor" of 1.42 [33] to correct for the assumption that the non-circular fibres have a characteristic diameter. Hence a fibre assumed to have a solid circular cross section and a modulus of ~30 GPa, would have a true modulus of ~42 GPa. The over prediction of the fibre modulus arises from the unknown relative volume fractions and angles above, especially for the S3 layer which will make only a small contribution to the fibre modulus.

Conclusion

The authors have previously proposed that the rule-of-mixture should include a fibre diameter distribution factor. In this article, an equation is proposed which should produce a value between 0 and 1 to reflect the decrease in fibre modulus with increasing fibre diameter. Equation 4 should permit the prediction of the elastic properties for all fibre composites, especially where the modulus is a function of the fibre "diameter." For fibres where the modulus is independent of diameter, the FDDF will be 1 and hence the new Equation reduces to the traditional form given above as Eq. 1. Moreover, Eq. 4 recognises the possibility to improve the structural performance of natural fibre composites through selection of fibres based on their "diameter." Whilst fibre diameter is likely to be less controllable than either fibre length or orientation, to achieve further gains in fibre stiffness (and ultimate strength and strain to failure) it is conceivable that, in the future, fibres might be produced such that the fibre diameter distribution factor is maximised.

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