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ANNIVERSARY REVIEW

Defects in natural fibres: their origin, characteristics and implications for natural fibre-reinforced composites

Mark Hughes

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Abstract This article reviews defects in natural fibres and how, ultimately, they affect the properties of composite materials reinforced with such fibres. Under ideal circumstances, certain natural fibre like flax and hemp can display excellent tensile mechanical properties. However, the potential of the fibre is generally not realised in natural fibre-reinforced composites. Partly, this poor performance can be explained by the presence of defects in the fibres known variously as dislocations, kinks or microcompressions. After briefly considering the chemistry and structure of plant fibres, the properties of selected natural fibres are reviewed. The origin of defects and the impact that processing has on their presence is then considered. The effect that defects have on the mechanical properties of bast fibre and their susceptibility to chemical degradation is also reviewed. Finally, the effect that dislocations have on the properties of composites reinforced with natural fibres is discussed and areas of potential further research needed are highlighted.

Introduction

The last two decades or more have seen resurgent interest in natural vegetable fibres, of both wood and non-wood origin, as reinforcement in polymer matrix composites. Initially the interest was mainly academic, but this soon gave way to commercialisation and to the introduction of natural fibre-reinforced composites (NFRCs) in, for example, automotive and construction applications. A major driver for using natural fibres is their perceived lower environmental impact—renewability, recyclability and biodegradability—along with their low density and the exceptional mechanical properties that have been reported for several fibre types [1, 2]. Although, some recent research has cast doubt on the true environmental advantages of using certain natural fibre types [3–5], and clearly there is still need to conduct quantitative analyses of the environmental impact of NRFCs, research into their use as composite reinforcement has continued to increase as evidenced by the growing number of publications appearing every year in the scientific literature. This has prompted the compilation of several review papers covering all aspects of research from the fibres themselves [6] to the properties and characteristics of composites reinforced with such fibre [7–9]. Indeed, one of the earliest review papers to cover NRFC materials science appeared in this journal a decade ago [10], exemplifying the research activity on NRFCs around the turn of the century. However, despite the undoubted attraction of using natural fibres as composite reinforcement and the research that has been, and is being, conducted on this topic, their use is still limited to mainly non-structural applications such as interior lining components for cars or lightly loaded garden decking materials. This, at first, seems slightly surprising given that the properties reported for some of the fibre types are excellent and comparable with those of manmade fibres such as glass fibre, and indeed plant fibres have been touted as replacements for glass fibre [1]. The reasons for the often mediocre properties of NRFCs, despite the theoretical potential of the fibres themselves, are not always clear; however, the inherent properties of the fibres themselves, the reinforcement architecture and the interaction between fibre and matrix are unquestionably contributory factors.

M. Hughes (✉)
Department of Forest Products Technology, Aalto University School of Chemical Technology, P.O. Box 16400, 00076 Aalto, Finland
e-mail: mark.hughes@aalto.fi

It is well known that the properties of a composite are, to a large extent, governed by the reinforcement architecture, that is to say the geometry of the reinforcement, the orientation of the reinforcement relative to the stresses applied to the composite, the reinforcement packing arrangement and its volume fraction, as well as the properties of the fibre–matrix interface. The fibre volume fraction (V_f) is probably the single most important factor affecting a composite's properties [11]. Many NRFCs have hitherto been reinforced with non-woven natural fibre structures [12] or with woven textiles produced for apparel or other such purposes, rather than specifically designed for composites. In these formats, the reinforcement architecture is poorly optimised—the fibre volume fractions are generally low and the fibre alignment and packing arrangement inefficient—thus many of the resulting composite mechanical properties tend to be inferior to their glass fibre-reinforced counterparts at comparable V_f [8]. In addition to the reinforcement architecture, the properties and structure of natural fibres are highly variable and this also significantly affects the behaviour of composites reinforced with such fibre. In a recent review for example, the adverse effect of fibre defects on the properties of NFRCs was highlighted [8]. Moreover, natural vegetable fibres are hydrophilic and as such they are not only subject to dimensional changes with varying moisture content, but they are also not particularly compatible with many polymeric matrices. Much research work has, therefore, been conducted over the years to tailor both the surface and bulk properties of natural fibres by modification, to improve their dimensional stability, reduce biodeterioration and to improve compatibility with polymer matrices, and several review papers on this topic have appeared in the literature [13–15]. On the other hand, the properties of the fibres themselves, and particularly the impact of fibre damage and fibre morphology, on the properties of these composites has received rather less attention; however, the impact on composite properties is, potentially, great.

The objective of this review is to cover the origin and characteristics of fibre damage in both wood and certain non-wood fibres that are of interest as potential composite reinforcement and to consider how this impacts upon the fibre properties and upon the composites reinforced with these fibres. The intention is not only to draw attention to some of the problems associated with using natural vegetable fibre as reinforcement, but also to highlight possible strategies for overcoming some of the worst effects.

Natural vegetable fibres

Natural vegetable fibres can be broadly categorised as either wood or non-wood and both have been used in composites. In wood, a fibre is a single cell and its properties are largely dependent upon type of cell and its function in the tree (e.g. mechanical support, conduction, storage or a combination) and this in turn is dependent upon the trees species. For example, in softwoods (and hardwoods) specialised cells known as tracheids perform the dual functions of providing mechanical support and conduction. Non-wood 'fibres' are generally collections of individual cells and can be classified according to where in the plant they are to be found [16]. Non-wood fibres may be seed hairs such as cotton, leaf fibres such as sisal, fruit fibres such as coir or the so-called bast fibres such as flax (*Linum usitatissimum*), hemp (*Cannabis sativa*) and jute (*Corchorus capsularis*). Bast fibres are obtained from the inner bark or phloem of the fibre bearing plant (Fig. 1) and are amongst the strongest and stiffest of all vegetable fibres and for this reason they are of particular interest as composite reinforcement.

Bast fibres are collections of elementary fibres (single cells) or 'ultimates' that are characteristically very long (2–5 cm for flax, compared with say 2–3 mm for softwood tracheids) and have extremely thick cell walls, being from 5 to 15 μm [17]. In diameter, ultimates vary from around 15–35 μm in flax, giving rise to an aspect ratio of around 1200 [18]. Collections of between one and three dozen ultimates form the fibres, generally referred to as 'fibre bundles' or 'technical fibres' that are extracted from the stem and that are used in technical applications such as textiles or composites. In flax, the length of the technical fibres varies from 0.3 to 0.6 m, whilst in hemp they range from 0.9 to 1.8 m [18]. The thickness of the technical fibres range from around 50 to 500 μm in flax and from 0.5 to 5 mm in hemp [18]. Much of the following discussion relates to bast fibres, though the chemical composition and structure of all natural vegetable fibres is similar.

Chemistry and structural organisation of the cell wall of natural fibres

Chemically, vegetable fibres consist of cellulose, lignin and matrix polysaccharides, including hemicelluloses and pectins, which are associated with the cellulose and lignin (Table 1). In addition to these there are a number of non-structural components including waxes, inorganic salts and nitrogenous substances [19, 20]. Cellulose is a high molecular weight, long chain molecule consisting of β-D anhydroglucopyranose units, bonded with β-(1 → 4) glycosidic linkages [19–21] and, with an axial Young's modulus reported to be in the region of 135 GPa [22] is analogous to the reinforcement in a fibre-reinforced composite. In the cell wall, cellulose is present mainly in the form of highly ordered bundles of cellulose polymers

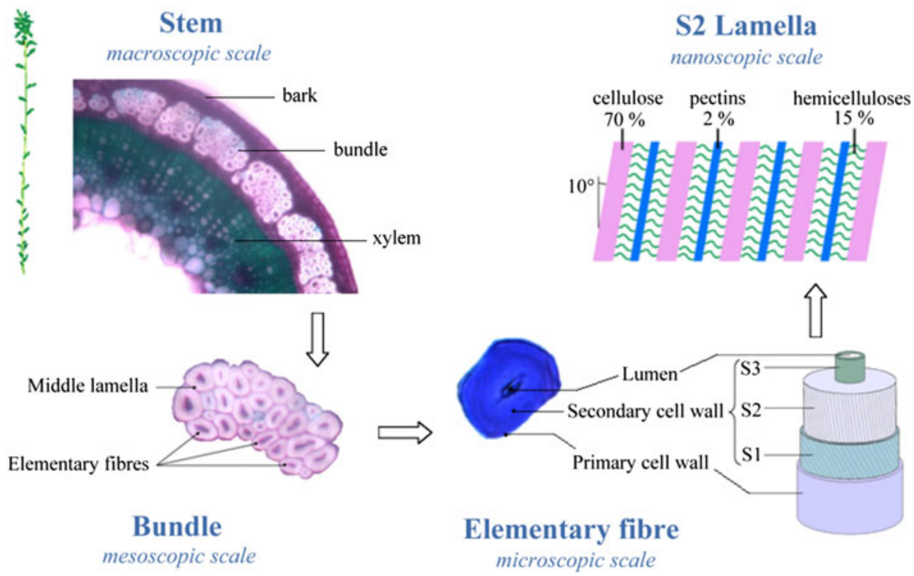

Fig. 1 Cross-sections and schematic representation of flax at different scales, from the stem to the ultrastructure [89]

Table 1 A summary of the main chemical constituents of flax and hemp fibre (various references)

Fibre type	Cellulose (%)	Hemicellulose (%)	Pectin (%)	Lignin (%)	Extractives[b] (%)	Reference
Flax	80–90	–	2–6[a]	–	3–4	[18]
	79	20.7	2.6	2.4	1.9	[23]
	71.2	18.6	1.1	2.2	6	[24]
	81	14	2	3	–	[25]
Hemp	85.7	–	10.2[a]	–	5.3	[18]
	83.4	20.1	1.0	4.1	0.9	[23]
	74	18	1	4	–	[25]

[a] Includes 'pectose bodies, lignin', 'pectose and gummy substances' and 'incrusting and pectin matter'. These include hemicellulose, pectin and lignin

[b] Substances extractable by organic solvents

known as microfibrils which are embedded in a matrix of other polysaccharides and lignin.

Within the cell wall (Fig. 1), the microfibrils are arranged helically in concentric lamellae. The winding angle of the microfibrils relative to the fibre axis in the dominant S2 layer of the secondary wall strongly influences the axial tensile properties of the fibre. The remaining layers of the secondary wall, the S1 and S3, occupy a much smaller volume and, unlike the S2 layer in which the cellulose chains are arranged in a single right-handed helix, the S1 and S2 layers are composed of cellulose chains arranged in both left- and right-handed helices [19]. The S1 layer is thought to be important in controlling fibre stability in compression by limiting excessive lateral cell expansion, whereas the S3 layer is believed to resist hydrostatic pressure within the cell [26]; the combined laminate structure of the cell wall is considered to be of importance in controlling trans- and intra-wall crack propagation [27]. In spruce (*Picea abies*) wood tracheids, the winding angle in the S2 layer lies generally in the range 10°–30° [19], whereas in bast fibres such as hemp it has been reported to be less than 10° [28] and even as low as 2°–3° [29]. The influence of the S2 winding angle is significant. Page et al. [30] demonstrated experimentally that a strong relationship exists between the elastic modulus of wood pulp fibres and the winding angle of the S2 layer (Fig. 2). Since low winding angles are associated with higher strength and stiffness [31], bast fibres would seem to be good choice as composite reinforcement.

Physical and mechanical properties of fibres

The density of cell wall material has been determined by several researchers [32, 33] to be of the order of 1500 kg m^{-3} and is relatively independent of species. The wall surrounds the central void space of the cell known as the lumen and clearly fibres having small lumens will possess a higher overall density than those having large ones. Thygesen et al. [34] observed that in some hemp fibres, the remaining lumen space in mature fibres amounted to less than 10% of the fibre cross-sectional area, indicating a fibre density in the region of 1350 kg m^{-3} and such values have been reported [35]. The high proportion of cell wall material, coupled with the high percentage of the reinforcing cellulose and their low winding angle relative to the elementary fibre axis lend the fibres good mechanical properties.

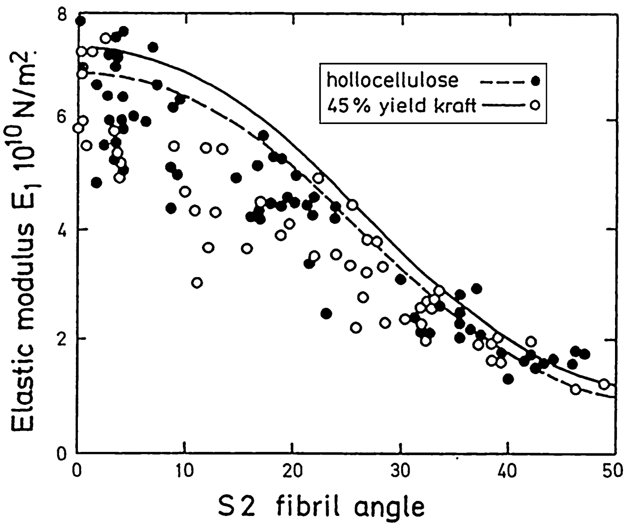

Fig. 2 Variation of the fibre elastic modulus with the microfibrillar angle of the S2 layer [30] (© TAPPI)

A summary of the reported tensile properties of flax and hemp is presented in Table 2. As with the chemical composition (Table 1) a great deal of variability exists in the values reported for any particular fibre type. This variability is the result of any one or more of a large number of factors, including:

- Fibre type; whether it is the technical fibre or fibre ultimate that is being tested
- Fibre variability; arising from ultrastructural organisation, growth conditions, the position of fibre in the stem, fibre maturity or harvesting
- Fibre damage; whether the fibres have been carefully removed from the stem in the laboratory or processed industrially
- Testing; the accuracy of the testing equipment, the type of test, measurement of specimen cross-section, number of replicates, gauge length, ambient humidity and temperature of test etc.

Table 2 The mechanical properties of flax and hemp fibres (various references)

Fibre type	Young's modulus (GPa)	Tensile strength (MPa)	Strain to failure (%)	Reference
Flax	–	814	–	[36]
	–	1500[a]	–	[37]
	103	690	–	[38]
	85	2000[a]	–	[1]
	50–70	500–900	1.3–3.3	[35]
	100	1100	2.4	[23]
	52	621	1.33	[39]
	19	649	–	[40]
	–	264–613	–	[41]
Hemp	–	690	–	[36]
	25	895	–	[1]
	30–60	310–750	2–3	[35]
	–	690	1.6	[23]
	57	–	–	[38]
	9	1080	–	[40]
	17–19	368–482	2.5–3.0	[42]

[a] Fibre ultimate

Fibre defects: dislocations, kinks and microcompressions

Despite the excellent theoretical mechanical properties and the potential shown in the laboratory of carefully isolated fibres, composites reinforced with these fibres do not, in general, reflect these properties. Partly, this can be attributed to functional characteristics and defects that affect the properties of the fibres. Unlike manmade fibre like glass, the structure of natural vegetable fibres is extremely heterogeneous and they possess certain anatomical features such as pits (openings in the cell wall of wood fibres that facilitate the movement of water in the living tree), as well as defects, that affect their properties. Dislocations and other fibre defects such as microcompressions, curls, crimps and kinks have, for instance, been shown to affect the properties of paper [43]. In single wood pulp fibres, these features have been shown to lead to non-linear stress–strain behaviour, with strain concentrations occurring in their vicinity, as well as near other strain risers such as bordered pits [44]. In non-wood fibres, such as flax and hemp similar defects have also been shown to affect fibre properties [39, 45].

In papermaking, the presence of dislocations in pulp fibres has a marked effect upon the fibre properties, and their origin, characteristics and importance has been reviewed by Nyholm et al. [46]. Under cross-polarised light, kink bands in the cell wall that are formed during compression failure of wood are clearly visible due to a change in birefringent properties [47]. Similarly, defects in the structure of flax and hemp (Fig. 3), also sometimes referred to as slip planes, microcompressions, nodes or dislocations, may be observed using polarised light microscopy [48]. The origin of these defects is not entirely clear, but they have been observed in hemp fibres carefully extracted from stem grown under wind-free conditions; moreover, plants placed under stress (wind or drought) exhibit an increase in the number and severity of the defects [49]. Bos and Donald [50] studied the deformation of single flax fibres using ESEM and observed that when a loop in a flax fibre was drawn tight, compression stresses on the inside of the loop induced failure by kinking and

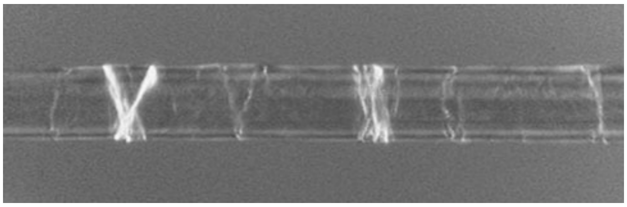

Fig. 3 An unprocessed hemp fibre ultimate under cross-polarised light (×100 magnification). The dislocations appear as light bands traversing the fibre [76] (© Koninklijke Brill NV)

from this they were able to derive a compressive strength of 1200 MPa. Baley [51] also noted the formation of kink bands on the compression side of flax fibres in bending. Compressive failure taking a similar form has also been observed in manmade fibres such as Kevlar 49 [52] and other high performance polymer fibres [53]. Interestingly, however, the difference between the tensile and compressive strengths of flax fibres is far less than that observed in manmade fibres. For example, Bos et al. [54] found that flax fibres displayed axial tensile strengths of around 1500 MPa whilst in compression, the strength was around 1200 MPa; in other words, the compressive strength of flax fibres is around 80% of the tensile strength, which compares with around 20% for Kevlar [55].

Kinking is also observed in unidirectional polymer matrix composites under compression parallel to the axis of the fibres [56]. Argon [57] proposed a model for the initiation of kinks in such materials. At the onset of instability, it was predicted that the compressive stress, σ_{comp}, would be given simply by:

$$\sigma_{comp} = {}^{\tau_s}/_{\Delta\Phi}$$

where τ_s is the plastic shear strength of the matrix and $\Delta\Phi$ is the average misorientation angle of the reinforcing elements (in radians).

If, as proposed by Argon [57], compressive strength is governed by the plastic yield strength of the matrix, it would seem reasonable that the matrix of polysaccharides and lignin present in bast fibres would confer greater stability and resistance to kinking than in synthetic polymeric fibres and this contention is supported by the findings of Bos et al. [54]. Synthetic fibres do not possess a 'matrix', but rely instead on weak Van der Waal's forces for interfibrillar bonding and it has been found that in synthetic polymeric fibres, improved compressive properties can be achieved by artificially introducing a 'matrix' through polymer infiltration [55].

Damage during processing

Although, bast fibres are likely to be better in compression than the aforementioned synthetic fibres, it seems that they too are prone to kink band formation during compressive loading. During the extraction of bast fibres from the stems they undergo several processes designed to separate the fibres from the core tissue (known as 'shive') of the plant and to clean and align the fibres in a process known as 'carding'. It is hardly surprising then that during processing, the fibres are subjected to large bending deformations that could lead to kink band formation. This supposition has been borne-out in a recent study in which the number of defects in flax fibres subjected to various processing steps was quantified, with a higher number of processing steps leading, not unsurprisingly, to more fibre damage [58]. Given that fibre defects are present even in fibres carefully extracted from the stems and that current processing methods cause damage to the fibre, there is clearly the need to develop processing methods that reduce the amount of damage induced. This necessity was recognised by Bos et al. [54], who also observed that individual, defect-free, fibres displayed exceptional properties but that the processing method used had a significant effect upon the fibre properties.

The effect of defects on mechanical properties

The influence of defects on the properties of wood fibres, particularly wood pulp fibres, has been widely studied over the years. Dinwoodie [59], for instance, studied the properties of wood fibres that had been isolated from precompressed wood containing kink bands and found that the fibres exhibited failure loads around 46% that of undamaged fibre, as well as reduced stiffness. In wood pulp fibres kink bands, most probably resulting from the pulping process and subsequent handling, have been shown to have reduced fibre tensile strengths and moduli [43, 60]. Interestingly, by drying wood fibres under tension kink bands and other such defects may occasionally be removed, resulting in improved tensile properties [61]. In addition to lowering the tensile stiffness and strength of fibres kink bands in wood fibres have been noted to act as critical defects in the fibre structure [43, 60] leading to fibre fracture, which has been successfully explained in a probabilistic manner [62, 63]. Another feature of kink bands (as well as other features, such as pit apertures, creases etc.) is that they can affect the surface strain distribution in single wood pulp fibres [44], with strain concentrations occurring in their vicinity. Defects in wood pulp fibre not only affect the properties fibres themselves, but also affect the properties fibre networks. For instance, it has been shown that the elastic modulus of paper is reduced by the presence of kink bands as well as other defects such as crimps and curls [43].

Davies and Bruce [39] studied the tensile mechanical properties of individual flax and nettle fibre ultimates at relative humidities ranging from 30 to 70%. Using a bespoke tensile testing apparatus, they demonstrated that the static and dynamic tensile modulus of the fibres decreased with increasing fibre damage, which they measured as the percentage of the fibre showing bright under a polarising microscope (it should be noted that the measurement of fibre damage was qualitative, since it was not possible to measure the degree of fibre damage). This loss in stiffness as the relative amount of fibre damage increases would imply that the damage acts as a form of strain concentrator and that, as the fibres are strained, there might be a tendency for the defects to straighten out and for the fibres to undergo strain hardening. Thygesen et al. [28] investigated the effect of dislocations on the tensile behaviour of hemp fibre ultimates. During testing, at a relative humidity of 65% and 20 °C, they observed that the dislocations disappeared as the fibres were loaded but that there was no noticeable strain hardening effect. However, they supposed that this was most likely due to the fact that this phenomenon was not discernable, rather than the kinks having no effect on the stiffness of the fibres. Hornsby et al. [64] reported that strain hardening took place in some flax fibre ultimates whilst undergoing tensile testing. In their study, single flax fibres had been isolated by pulping in a co-rotating twin screw extruder and conditioned at a relative humidity of 10–15% and temperature of 23 °C before testing. Baley [45] later reported that flax fibre containing kink bands underwent non-linear straining behaviour during tensile testing; following an initial linear region, the fibres appeared to undergo plastic deformation before strain hardening as the test continued followed by a final linear region. After repeated loading–unloading cycles, this 'S' shaped non-linear behaviour disappeared and the fibres displayed essentially Hooekan behaviour. Such non-linear behaviour is well known in synthetic fibres that undergo a similar form of compression failure. DeTeresa et al. [52], for example, observed that Kevlar 49 fibres that had been previously compressed underwent considerable extension with almost no increase in load in a tensile test as the kink bands straightened out, followed by a rapid increase in stiffness. Indeed, they commented that the prior compression of the fibre had little effect on the fibres save for a small drop in tensile strength. Interestingly, Nilsson and Gustafsson [65], who used finite element analysis to model the properties and behaviour of natural fibres containing kink bands, showed that the fibres would undergo strain hardening during tensile loading and they obtained good agreement with the experimental data of Baley [45]. They also concluded that the S-shaped stress–strain response of fibre containing kink bands resulted from 'local rotations of the fibre as a consequence of plastic shearing of the hemicelluloses. The rotation straightens the dislocated cellulose fibrils, which in turn increases the stiffness of the fibre.' Baley [45] also concluded that non-linear behaviour in flax fibre at low applied strains may have been the result of kinks tending to straighten out.

The effect that kink bands have on the strength properties of the fibre is less clear. Baley [51] investigated the relationship between the number of defects and the tensile strength of flax fibre ultimates, finding no clear evidence for a relationship between the two parameters. On the other hand, a negative correlation between fibre diameter and tensile strength was observed. During tensile tests conducted in a scanning electron microscope, transverse cracks in the fibres were observed at the kinks, though as these were only observed on the surface, it was not possible to be certain of damage within the main bulk of the cell wall. Davies and Bruce [39] concluded that the probability of fibre failure increased at a given load with increasing fibre damage, whilst Andersons et al. [63] described strength in terms of the number of defects in the fibre. It is perhaps worthwhile recalling that Bos et al. [54] reported tensile strengths of 2500 MPa for certain individual flax fibres carefully extracted from the stem and in one instance a tensile strength of 4200 MPa was obtained.

Clearly, there is the potential to obtain natural fibres with excellent tensile properties however it also seems probable that the introduction of damage during the isolation process may reduce these significantly. This is exemplified by the study done by Aslan et al. [58] who investigated the effect of processing in the presence of defects and the tensile strength of flax fibre, finding that processing reduced the tensile strength from an average of 1445 MPa for technical fibre carefully extracted from the stem to 812 MPa for industrially processed technical fibre.

Increased chemical reactivity

There is some evidence emerging to suggest that in addition to the aforementioned effects on the fibre mechanical properties, kink bands are also more chemically reactive regions in the fibre and this could have a significant impact on fibre properties if they undergo any additional chemical processing, for example, to improve fibre–matrix adhesion, or to stabilise the fibre. Fibre modification is an extensive area that has, as mentioned previously, been the subject of several reviews in recent years [13–15]. Moreover, this could be problematic if the aim is to separate the technical fibres of say flax or hemp into the individual cells or 'ultimates'.

Thygessen [66] proposed that acid hydrolysis could be used as a means of quantifying defects in hemp fibres, supposing that hydrolysis would take place preferentially at the dislocations and in wood pulp fibres there is evidence for greater reactivity at dislocations [46]. Dinwoodie [59] postulated that the decrease in tensile strength is a manifestation of damage to the cellulose molecule. In the zone of the kink, the cellulose chains are bent in the form of a sharp 'Z' and it is believed that this results in a loosening of the structure, with the severance of cross-bonds in the unit cell and possibly a limited amount of breakage of the longitudinal covalent bonds [59]. It would certainly seem as though structural alterations take place in the kinked zone, since it has been reported that increased chemical reactivity in wood fibre, uptake of dyes etc. occurs in these regions [67]. It is possible that in addition to lateral, interfibrillar bond scission, some damage to the longitudinal covalent bonds, as postulated by Dinwoodie [59] may also take place. Interestingly, in a study on kink band formation in rigid-rod polymers, using low-dose high resolution electron microscopy, it has been shown that at the juncture between undisturbed fibrils and those lying in the kinked zone, very large angle changes in molecular orientation (40°) at very sharp (0.5 nm) tilt boundaries are observed [68]. It has been calculated that a radius of curvature of ~9 nm is sufficient to cause damage to the cellulose microfibril [69] giving rise to the possibility, at least, that some cleavage of the cellulose chains might take place. If similar kink conformations were to occur in damaged bast fibres, it is then perhaps reasonable to suppose that localised axial damage to the cellulose molecules may occur. In a recent study on dislocations in hemp fibre by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), Dai and Fan [70] reported a crystallinity index obtained by FTIR of 41.3% in the dislocations compared to 48.4% in un-defected parts of the fibre. They also claim a reduction in the amount of hemicelluloses at the sites of the dislocations. Hänninen et al. [71] measured the intrinsic viscosity of flax fibre that had undergone varying degrees of commercial processing corresponding to differing levels of mechanical damage. Intrinsic viscosity is commonly employed in the pulp and paper industry as a means of evaluating the degree of polymerisation (DP) of cellulose [72]. Hänninen et al. [71] observed that with increasing mechanical processing the intrinsic viscosity increased, consistent with the removal of low molecular weight species associated with hemicelluloses and, moreover, indicating that there was at least no severe scission of the cellulose chains resulting from simple mechanical action. Following acid hydrolysis of the fibres, however, a marked reduction in viscosity was observed and that this reduction increased with increased mechanical processing, thus indicating that scission of the cellulose chains had occurred. It was supposed that this scission occurred in the defected regions of the fibre.

It seems clear that defects in fibres affect not only their mechanical properties, but also the susceptibility of the fibres to chemical attack. Both have potentially severe effects on the properties of composites reinforced with such fibres. So, what are the implications of these defects on composite properties?

The influence of fibre defects on composite properties

It is probable that heterogeneous fibre strain distribution caused by kink bands in the fibre, coupled with the distinct geometry of defects themselves could well lead to stress concentrations occurring in polymeric matrices when used as reinforcement. In turn, these stress concentrations could promote crack formation at the interface, leading to fibre–matrix de-bonding and to localised rupture of the matrix. Parallels can be drawn with work carried out on the effects of residual thermal stresses in high-modulus polyethylene fibre composites. In these composites, it has been found that kink bands formed in the fibres as a result of axial curing stresses, as well as pre-existing damage, had the effect of creating stress concentrations in the matrix in the vicinity of the kinks which were thought to act as sites of potential crack initiation and fibre–matrix de-bonding [73]. More recently, Gonzalez-Chi et al. [74] studied the effect of kink bands in Twaron 2200 fibres embedded in a low density polyethylene film strained in tension parallel to the fibre axis and, by using Raman spectroscopy, were able to measure the axial fibre stress in the region of kink bands. They found that the axial fibre stress reduced in the kink band in accordance with a generalised shear-lag model and concluded that 'a kink band acts as a complex local stress concentration.' In hemp fibre-reinforced composites, Eichhorn et al. [75] observed strain-induced shifts in the Raman spectra of flax and hemp fibre and accorded the large variability in the shift sensitivity of individual fibres of the same fibre type to the presence of kink bands. They also showed that these defects gave rise to stress concentrations in an epoxy matrix when the defected fibres were used as reinforcement. Using half-fringe photoelasticity, Hughes et al. [76] were able to quantify stress concentrations in an epoxy matrix in the vicinity of kink bands in strained single hemp fibre composites. Stress concentrations of up to 1.4 were noted in close proximity to the kink band (Fig. 4). It was postulated that the defects could act as crack initiation sites and matrix microcracks were indeed observed near to the location of the kink bands.

In a later study by Hughes et al. [77], it was shown that in unidirectionally aligned flax fibre-reinforced unsaturated polyester composites with a V_f of approximately 60%, the composites displayed distinctive non-linear tensile stress–strain behaviour. Following a small linear region, the composites exhibited a distinct 'knee' in the stress–strain curve, which the authors attributed to a yield point. Continued straining was accompanied by strain-softening

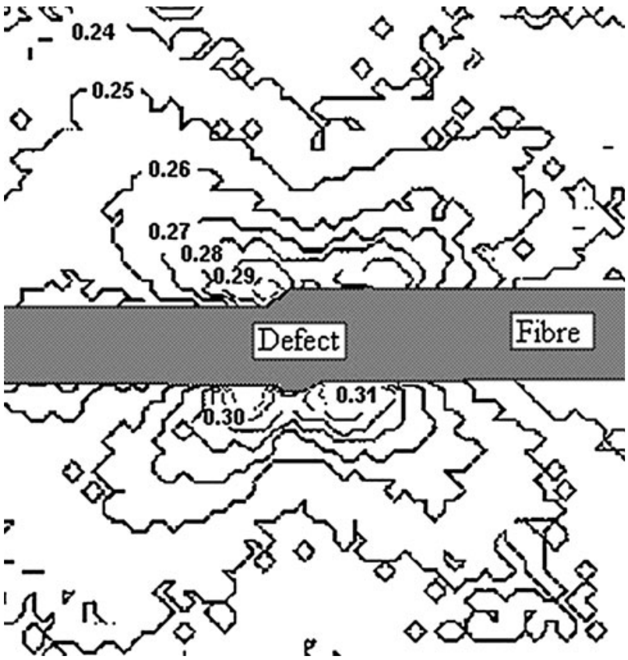

Fig. 4 A contour map of partial fringe order in an epoxy matrix around a fibre dislocation in a strained single fibre composite [76] (© Koninklijke Brill NV)

followed later by strain hardening before failure. A comparable E-glass fibre-reinforced composite displayed linear stress–strain behaviour to failure. Acoustic emissions analysis was employed to monitor failure events taking place during the straining of the composites. Acoustic events were noted to occur in the region of the yield point although it was not possible to attribute specific failure events to the emissions. By using both unmodified flax fibre, and fibre modified by propionic anhydride and methacrylic anhydride to alter the degree of adhesion between the fibre surface and the unsaturated polyester matrix, it was shown that the yield point could be shifted and the post yielding behaviour altered. From this, the authors postulated that defects had the effect of 'segmenting' the fibres in such a way that they acted as a series of shorter fibres joined by the defects; altering the degree of interfacial adhesion affected the composite strain at which interfacial de-bonding took place, thereby altering the yield point. Similar behaviour has recently been observed in Charlet et al. [78], who likened the stress–strain behaviour of unidirectional composites (which as in Hughes et al. [77] was flax fibre in an unsaturated polyester matrix) to that of the stress–strain behaviour of the reinforcing fibres. They too noted a change in the slope of the stress–strain curve at a strain of around 0.3% (similar to the strain at the 'yield' point observed by Hughes et al. [77]), which they attributed to failure of the thin external layer of the fibre. The contention that the defects act in the way so as to 'segment' the fibres so that they act as a series of short, stiff fibres joined regions of lower stiffness at the defects has to some extent been verified by Eichhorn et al. [10], who demonstrated that shear stresses in the matrix parallel to the surface of a bast fibre follow a 'Cox-type' shear-lag profile.

If the kink bands do affect the deformation behaviour of unidirectional composites as described above, then this could have serious implications for composite materials reinforced with such fibre. The onset on inelastic behaviour at low levels of applied stress would result in composites that would undergo plastic deformation making it difficult to see where they would find application in more highly loaded situations.

A further potential problem relating to the structural use of NFRCs is their poor toughness relative to glass fibre-reinforced equivalents. This may be problematic in certain application, but may not be an issue in all situations. On an equal fibre volume fraction basis, the measured work of fracture of a thermosetting matrix NFRCs has, for instance, been reported to be an order of magnitude lower than an equivalent glass fibre-reinforced material [79]. This too has been linked the presence of defects in fibres [80, 81]. Defects affect the morphology of the fibres and, together with their irregular cross-section ensure that the fibres are well 'keyed' into the surrounding matrix. As a result fibre pull-out, considered to contribute substantially to the overall work of fracture of a composite [56], is suppressed. In wood, a major contributor to overall toughness is thought to be a pseudo-plastic tensile buckling mechanism first proposed by Gordon and Jeronomidis [82]. This mechanism is closely associated with the microfibril angle of the S2 layer, with toughness increasing with increasing microfibril angle to a certain point. This mechanism has been verified using synthetic analogues of the wood cell wall [83]. In bast fibres, which have a very low S2 layer microfibril angle, this mechanism is presumably suppressed so little contribution to the overall work of fracture is to be expected from this mechanism. Whatever the reasons for the relatively low toughness are, further research is justified in trying to understand the underlying mechanisms in NFRCS.

Prospects

Gordon Aerolite, a material made from unidirectionally aligned skeins of unbleached flax thread compression moulded in a matrix of phenolic resin, was developed in the 1930s and 1940s [38, 84, 85]. Even today, the properties of this material remain impressive: a tensile strength of 480 MPa, a Young's modulus of 48 GPa and a compressive strength of 200 MPa [84]. Clearly, there is potential to produce composites reinforced with bast fibres with seemingly excellent properties, however, it is equally clear that a number of researchers have recognised that damage to the fibre caused either during growth or during subsequent processing affects not only the fibre properties but also the properties of composites reinforced with these fibres. If natural vegetable fibres are to be used in composites with greater load-bearing capacity, it appears evident that research efforts should be directed at finding ways reducing the occurrence of defects as well as better understanding their effect on composite properties and seeking ways of minimising their influence.

It seems clear that a radical re-think of how fibres are grown and processed in the first place may be needed. Evidence suggests that the growing conditions [66] influence the occurrence and severity of defects. Moreover, it is also clear that the method of decortication plays a role in determining the damage introduced into the fibre. Bos et al. [54], for example, showed that careful decortication by hand resulted in fibres with far fewer defects, whilst Aslan et al. [58] clearly demonstrated that industrial processing methods result not only in a greater number of defects, but also fibres of lower strength. It also seems clear that it would be better to base the composites on the fibre ultimates, rather than on the technical fibres as they are likely to possess better strength properties (recall that individual fibre ultimates with tensile strengths exceeding 2 GPa have been recorded whereas in general technical fibre strength is generally no more than half this value). This supposition has been partly verified in a study by Stuart et al. [86], who demonstrated that by separating technical flax fibre into ultimates, a substantial improvement in the tensile strength (50%) of random mat-reinforced composites could be achieved. The strength improvement was attributed mainly to the separation of the fibres rather than to modification of the fibre surface.

Separating the fibre possibly brings about its own problems. It appears that fibre defects cause the fibres to be more chemically reactive at those sites and whilst the defects themselves appear to reduce the fibre strength and stiffness, there is no clear evidence to suggest that the cellulose chains themselves are being cleaved [71]. Nevertheless, the potential susceptibility of the defects to chemical attack, in particular acid hydrolysis, has been demonstrated by Thygessen [66] and by Hänninen et al. [71] and must surely be taken into account not only when trying to separate the technical fibres into ultimates but also when considering any form of physical or chemical modification (e.g. acetylation) in which the liberation of acid is likely to result in reduced fibre properties. If such modification is deemed necessary it would most probably be worthwhile performing such operations on fibre minimally affected by defects or by choosing separation techniques that are likely to result in less physical or chemical damage. Steam explosion has been explored in this respect and might be a possible solution [87]. Removal of the pectins binding the fibre ultimates together using enzymatic approaches combined with chelating agents have also been explored with some success [86].

One of the major drawbacks of utilising natural fibres in composites is currently the lack of suitable reinforcing textiles. Being of finite length, technical bast fibres generally need to be spun to provide continuous lengths for forming into aligned textiles. There are certain disadvantages with this. Traditional spinning techniques require the introduction of twist into the yarn to provide the frictional forces necessary to hold the yarn together. Twist, which effectively translates to off-axis fibres, is not ideal as reinforcement. Moreover, the shorter fibre ultimates (circa 25 mm in length) are more difficult to spin in the first place. In addition to this the spinning process itself may introduce further damage to the fibre [88] which, following the arguments above would be deleterious to composite properties. Moreover, spinning is an expensive process and adds significantly to the environmental burden of producing natural fibre reinforcement [4, 5]. Nevertheless, research efforts are needed to develop pre-form materials that harness the full potential of the fibre, without introducing significant additional physical damage or chemical degradation and recently at least two European level projects, including the NATEX—Natural Aligned Fibres and Textiles for Use in Structural Composites Applications—project (http://www.natex.eu) have been addressing this issue.

It is still not entirely clear how big an impact the defects really do have in a particular system, since only a relatively few fibre–polymer systems have been investigated. It is possible that the effects of defects are not so apparent in certain systems and may be largely ignored. However, it seems clear that further research into the effects of defects on the composite micromechanics is still needed. Nevertheless, despite the current shortcomings of NFRCs, certain technical properties, such as their low density, good specific stiffness as well as the potential environmental benefits, are of merit making further research into these materials most worthwhile.

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