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Deformation and fracture behaviour of flax fibre reinforced thermosetting polymer matrix composites

Mark Hughes · James Carpenter · Callum Hill

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Abstract The mechanical properties of unidirectional flax fibre reinforced unsaturated polyester resin composites were studied with particular emphasis on their tensile deformation behaviour. These materials displayed characteristic non-linear behaviour when loaded parallel to the axis of the fibre, with a distinct knee preceding a drop in stiffness. Further deformation resulted in strain hardening behaviour. Load cycling and acoustic emissions analysis were used to investigate the nature of the knee and it was found that this corresponded with yielding behaviour in the composite. A well-defined yield point could be identified, which in composites of around 60% fibre volume fraction, occurred at a strain of some 0.12% and a tensile stress of 32 MPa. Varying the interfacial properties, through chemical modification of the fibre prior to lamination, was found to have a marked effect upon the onset of yielding and the yield point itself, as well as the deformation and fracture behaviour of the laminate. It is considered that this behaviour is intimately linked to the straining behaviour of the fibre as well as the fibre–matrix interaction and hypotheses to explain the observed behaviour are presented.

M. Hughes (✉) · J. Carpenter
BioComposites Centre, University of Wales, Bangor, UK
e-mail: mark.hughes@tkk.fi

J. Carpenter · C. Hill
School of the Environment and Natural Resources, University of Wales, Bangor, UK

Present Address:
M. Hughes
Laboratory of Wood Technology, Department of Forest Products Technology, Helsinki University of Technology, P.O.Box 6400, Helsinki FI-02015 TKK, Finland

Introduction

In recent years there has been resurgent interest in the use of natural fibres as reinforcement in polymer matrix composites (PMCs). The greater consideration given to these, so-called, biocomposites has arisen because of a number of factors. These include the improved eco-profile of biocomposites, the renewability and potential sustainability of the raw materials as well as new market opportunities for industrial crops. Reports by a number of workers (summarised in Table 1) indicate that the tensile properties of certain natural fibres—in particular bast fibres like flax, hemp and jute—offer potential as reinforcement in true structural composite applications. To date, however, the applications for natural fibre reinforced PMCs have been limited to mainly non-structural situations such as car interior trim. There are a number of reasons why this should be, but perhaps two key features come to the fore. Firstly, the mechanical properties of biocomposite materials rarely fulfil the potential expected from a consideration of the reported properties of the fibres and secondly, there is uncertainty about the behaviour of the materials under both short- and long-term loading. It is believed that a significant factor in realising the greater use of biocomposite materials in load bearing applications is a fuller understanding of their mechanical behaviour. The work reported herein was instigated with the intention of gaining a fuller understanding of the deformation and fracture behaviour of flax fibre reinforced thermosetting PMCs and to explain the observed phenomena in terms of the material microstructure.

As may be seen from Table 1, the tensile properties of natural fibres vary considerably, influenced by many

Table 1 A summary of the mechanical properties of flax, hemp and jute fibre bundles and fibre ultimates, together with E-glass fibre

Fibre type	Young's modulus (GPa)	Ultimate tensile strength (MPa)	Strain to failure (%)	Reference
E-glass	76	2,000	2.6	[1]
Flax	–	814	–	[2]
	–	1,500	–	[3]
	103	690	–	[4]
	85	2,000	–	[5]
	50–70	500–900	1.3–3.3	[6]
	28	345–1,035	2.7–3.2	[7]
	100	1,100	2.4	[8]
	52	621	1.33	[9]
Hemp	–	690	–	[2]
	25	895	–	[5]
	30–60	310–750	2–3	[6]
	–	690	1.6	[8]
	57	–	–	[4]
Jute	–	455	–	[2]
	8	538	–	[5]
	10–78	–	–	[10]
	27.6	393–773	1.7–1.8	[7]
	13	550	–	[8]

factors including whether it is the fibre ultimate (individual cell) or technical fibre (a bundle of cells cemented together with pectins) that is being tested. Many natural fibres, including bast fibres, have been utilised as reinforcement in thermosetting polymers such as unsaturated polyesters and epoxies and the macromechanical properties of various composites systems have been reported in the literature [10–17]. In view of the importance of the interface in controlling the macroscopic properties of composites, a great deal of attention has been focussed on trying to elucidate the nature of stress transfer at the fibre–matrix boundary [18, 19] or in analysing the effects that microscopic fibre defects have upon the stress–strain field in the surrounding matrix [20]. Further, a great deal of attention has been paid to the chemical modification of the fibre surface to render it more compatible with the polymer matrix, or indeed to chemically bind the fibre to the matrix with the intention of improving either the short-term mechanical properties or longer-term environmental performance of the composite [16, 21–24]. Other workers have focussed on the influence that fibre parameters have upon the macroscopic properties of the composite [25, 26].

No studies, however, appear to have reported on the nature of the deformation behaviour of natural fibre-thermosetting polymer composite systems and how this relates to the structural application of these materials. Furthermore, whilst there has been a certain amount of work undertaken to characterise the deformation behaviour in model systems, such as individual fibre micro-tensile composites [18, 19], this has in general not been related to the bulk behaviour of the material. If confidence in these materials is to be given to design engineers it is vital that a full understanding, not only of the macroscopic behaviour, but also the relationship between microstructure and macro-properties of the composites, be achieved.

Recent work has indicated that inelastic, non-linear behaviour in bast fibre reinforced-unsaturated polyester composite systems occurs at relatively low values of applied stress and strain [17, 27]. Incipient irreversible processes in the composite occurring at low values of strain would undoubtedly have implications in terms of the structural use of such materials. In this study, the mechanical response of unidirectional flax fibre reinforced thermosetting polymer composite systems, with differing levels of fibre–matrix adhesion, was studied under quasi-static tensile loading in order to gain a fuller understanding of their mechanics and micromechanics of deformation and fracture, with particular emphasis on non-linear, inelastic, behaviour.

Experimental

Fibre

Linen grade flax fibre was obtained in the form of sliver (from SANECO, Zone Artisanale, 231 Ruelle Dufour, 59850 Nieppe, France). All fibre was solvent extracted with a mixture of toluene, methanol and acetone in the proportions 4:1:1 (by volume) in a Soxhlet extractor for 5 h to remove any waxy substances prior to use. This fibre was used in unmodified form (UnM) and in modified form (see section ''Fibre modification'').

Fibre modification

Fibre was modified by reaction with two reagents: (i) methacrylic anhydride and (ii) propionic anhydride. Fifty gram samples of Soxhlet extracted fibre were oven dried at 105 °C for 16 h and subsequently reacted in 1 M solutions of reagent in pyridine at 95 °C for 7 h. After quenching the reaction, the fibre samples were Soxhlet extracted to remove any unreacted reagent with a mixture of toluene, methanol and acetone in the proportions 4:1:1 (by volume) for a further 5 h prior to oven drying as before. The fibres modified using methacrylic anhydride were designated MeA modified fibre and those modified with propionic anhydride, were designated PrA modified fibre.

Lamination

Prior to lamination, both the modified and unmodified fibre was allowed to equilibrate under ambient conditions of relative humidity (RH) and temperature. Unidirectional composite bars, rectangular in cross-section and of nominal dimensions 450 mm × 25 mm × 3 mm were fabricated in a closed compression mould. Fibre volume fractions (V_f) were adjusted by varying the weight of fibre used in the initial lay-up. The required weight of fibre was initially vacuum impregnated with catalysed resin to ensure good wet out. The resin used was an unsaturated polyester (Wresipol 31466, Resinous Chemicals Ltd.), catalysed by the addition of 1% of an organic peroxide catalyst (Butanox M50, from Akzo Nobel). Laminates reinforced with unmodified and modified fibre were fabricated. Additionally, laminates reinforced with unidirectional E-glass fibre (from Scott Bader) were also prepared. The glass fibre reinforced laminates were laid-up in the mould, ensuring that the fibres were carefully aligned parallel to the long axis. Four millimetres thick sheets of pure, unreinforced polymer were prepared by casting catalysed, liquid resin between glass plates. All laminates and pure polymer samples were cured at room temperature overnight, followed by post curing at 50 °C for 45 min.

Sample preparation and testing

The cured laminates were trimmed to remove the ends, leaving 250 mm long tensile specimens for testing. Pure-polymer specimens were cut from the cast sheets with a water-cooled diamond saw. The nominal dimensions of the un-reinforced polymer specimens were 20 mm × 4 mm × 200 mm. The specimen width and thickness was measured to an accuracy of 0.01 mm with a digital micrometer, from which the cross-sectional area was calculated. Length was measured to an accuracy of 1 mm using a rule. The weight (to an accuracy of 0.01 g) of each specimen was recorded and the specimen density calculated. Aluminium end tags were glued with Araldite adhesive to the specimens. Prior to testing, all specimens were conditioned for at least 48 h at 65% RH and 20 °C.

Tensile tests were conducted on an Instron (model 1195) universal testing machine fitted with a 100 kN capacity load cell. The specimens were clamped using self-tightening jaws. Load and extension data were acquired digitally. Specimen extension was measured by an extensometer fitted, within the gauge length, to the specimen. Testing was conducted in accordance with BS 2782: Part 10: Method 1003:1977 (EN 61). The cross-head speed was 10 mm min^{-1}. Six pure-polymer specimens, 8 UnM fibre reinforced specimens, 4 each of the MeA and PrA modified fibre reinforced specimens and 4 E-glass fibre reinforced specimens were tested.

A number of further specimens reinforced with unmodified flax fibre were loaded to set points along the load–extension curve and subsequently unloaded. The loading–unloading cycle was recorded.

Acoustic emissions analysis

Selected tensile specimens reinforced with either E-glass fibre or UnM flax fibre were tested in uniaxial tension as outlined in section ''Sample preparation and testing'', at a cross-head speed of 1 mm min^{-1}. This lower deformation rate was adopted to enable the capture of data arising from acoustic events. The acoustic emissions (AE) produced when the specimens were deformed were detected by a surface mounted piezoelectric transducer and analysed on an MR1004 acoustic emission analyser. Further detail on the AE techniques employed is provided in Ref. [28]. AE events were sorted into 25 amplitude levels, each 2.4 dB wide.

Fractography

The tensile fracture surfaces of composite specimens were examined using a Hitachi S-520 scanning electron microscope. Samples were first mounted on aluminium stubs and gold coated using a Polaron SEM coating unit E5000.

Results

Chemical modification

The rationale for chemically modifying the fibre in the manner described in section ''Fibre modification'' was to explore the effect that fibre–matrix adhesion had upon the mechanical properties, particularly the deformation behaviour, of flax fibre reinforced unsaturated polyester composites. The purpose of pursuing this modification regime was not, therefore, an attempt to develop new natural fibre treatments for composite applications, rather, to vary interfacial adhesion so as to assist in the understanding of bast fibre reinforced polymer composite systems.

Activation of the fibre surface for subsequent co-polymerisation with the resin matrix was achieved by reaction with the di-functional methacrylic anhydride. This was expected to result in true chemical

bonding between fibre and matrix [16, 24]. Alteration of the fibre surface chemistry and hence surface energy by the introduction of a hydrocarbon surface coating was expected to render the fibre more hydrophobic and thus improve the wetability of the fibre by the liquid resin. This was achieved through reaction with propionic anhydride.

A scheme showing the reaction between the fibre hydroxyl (–OH) groups and (i) methacrylic anhydride and (ii) propionic anhydride is shown in Fig. 1. Modification through the introduction of reactive vinylic groups at the fibre surface by esterification of the flax –OH groups with methacrylic anhydride was expected to lead to subsequent radical co-polymerisation between these vinylic groups and the unsaturated bonds of the resin during lamination [24]. Unlike modification with methacrylic anhydride, propionic anhydride modified fibre does not contain a functional site for reaction with the resin matrix. However, alteration of the chemistry of the fibre surface, rendering it more hydrophobic, was thought likely to occur, leading to improved compatibility with a more hydrophobic polymer [24].

Fractography

Evidence for improved bonding between reinforcement and matrix using the modified fibre was provided by fractographic examination. Figure 2 shows the macroscopic failure observed in UnM (A), MeA (B) and PrA (C) flax fibre reinforced unsaturated polyester composites, respectively. In the case of the unmodified fibre reinforced material, failure invariably occurred through delamination and wide-scale debonding between fibre and matrix. With both the PrA and MeA modified flax fibre reinforced material the mode of failure was observed to change to one of brittle tensile failure.

Scanning electron microscopy (SEM) of the fracture surface of the UnM reinforced material (Fig. 3) revealed that there was apparently little adhesion between the fibre and matrix as evidenced by the extensive fibre separation from the encapsulating

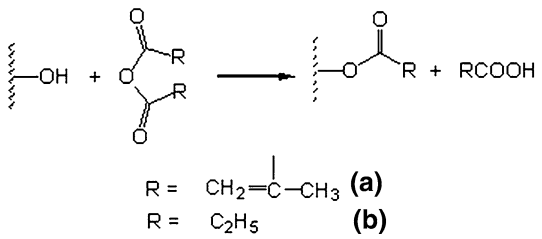

Fig. 1 The reaction mechanism between flax fibre –OH groups and (**a**) methacrylic and (**b**) propionic anhydrides

matrix (Fig. 3a) and river lines (Fig. 3b at i), as described by Hull [29]. More significant cracks, traversing the laminate by a distance of several fibre diameters, can be seen in Fig. 3b (at ii).

SEM of the fracture surfaces of the MeA and PrA modified flax fibre reinforced unsaturated polyester matrix composites (Figs. 4, 5) revealed that an intimate bond was formed between reinforcement and matrix. With both the MeA and PrA fibre reinforced materials, little fibre pullout was observed, with the fracture surfaces exhibiting a distinct ''blocky'' appearance (Fig. 4a, b). Close inspection of Fig. 4 does seem to suggest that there was somewhat greater pullout in the PrA fibre reinforced material together with a greater degree of inter laminar shear failure (Fig. 4b). This would be consistent with the lower adhesion that might be expected in this system. Strong interfacial bonding may be expected from the presence of, what appears to be, extensive fibrillation on the fibre surfaces of both the MeA and PrA modified flax fibre reinforced laminates (Fig. 5). This was most probably caused by regions of the fibre, well bonded to the matrix, being ''torn'' from underlying layers of the fibre. Improved interfacial adhesion between methacrylic anhydride modified hemp fibre and an unsaturated polyester matrix has been reported previously [16].

Laminate properties

Laminate density and fibre volume fraction

In view of the inherent variability of natural fibre and the difficulty in obtaining accurate data on fibre density, the following expression, which does not require a prior knowledge of the fibre density, was used to calculate the fibre volume fraction [11]

$$V_f = (V_c - (M_c - M_f)/\rho_r)/V_c \quad (1)$$

where: V_c is the volume of the composite laminate, M_c is the mass of the composite laminate, M_f is the mass of the fibre, ρ_r is the density of the cured polymer.

Laminates were fabricated to a nominal V_f of 0.55, however, the V_f of individual specimens varied from approximately 0.53–0.60 for the UnM flax fibre reinforced specimens, from 0.53–0.58 for the PrA modified fibre reinforced specimens and from 0.53–0.63 for the MeA modified fibre reinforced specimens.

Mechanical properties

Typical engineering stress–strain curves for the glass fibre, UnM, MeA and PrA flax fibre reinforced

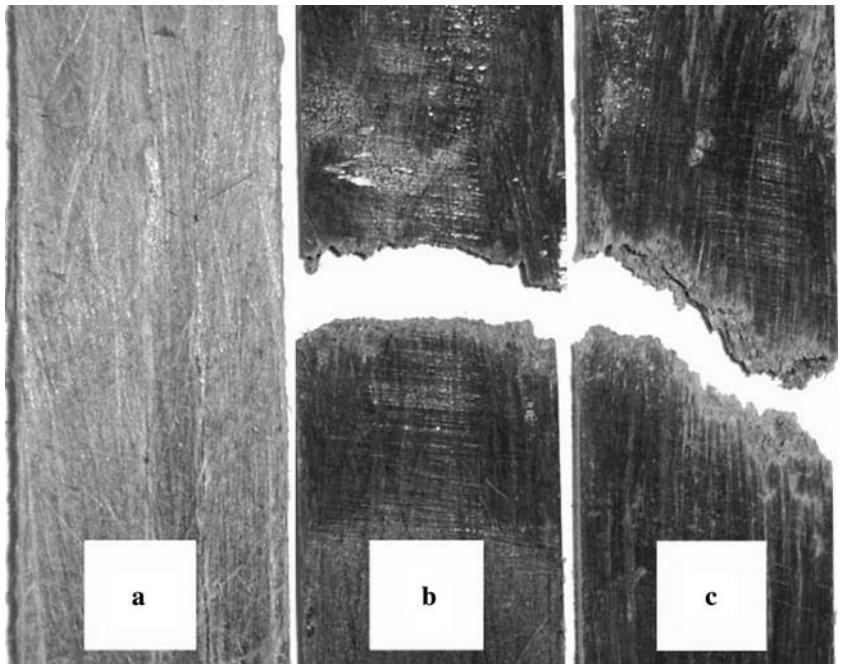

Fig. 2 Failed tensile specimens: (**a**) unmodified, (**b**) methacrylic anhydride and (**c**) propionic anhydride modified flax fibre reinforced unsaturated polyester laminates

unsaturated polyester matrix composites, along with the pure-polymer are presented in Fig. 6. As may be observed, the E-glass fibre reinforced material exhibited ostensibly linear behaviour up to the point of failure, at a strain >2% (for clarity, the curve for the glass fibre reinforced material has been truncated). The UnM flax fibre reinforced material displayed initially linear behaviour up to about 0.1% strain, at which point a distinct change in the gradient of the stress–strain curve was observed. Similarly, both the MeA and PrA modified materials showed initially linear behaviour, followed by a change in gradient which, whilst not as significant as that observed in the UnM flax fibre reinforced material was still apparent. The pure unsaturated polyester specimens displayed the characteristic behaviour of organic glasses, deforming linearly to the point of brittle fracture.

Whilst the volume fraction of the glass fibre reinforced material was approximately 26% lower than that of the natural fibre reinforced laminates, the density of the former was approximately 30% higher (see Table 2). When density was taken into account, the specific stiffness (E/ρ) of the natural fibre reinforced material was approximately 26% higher than that of the glass fibre reinforced material. This is significant and could have real benefits in practice.

Interestingly, little difference between the Young's modulus of the UnM flax fibre reinforced laminates and that of the PrA and MeA modified fibre reinforced material was noted. Indeed, what variation there was between the modified and unmodified fibre reinforced laminates could be accounted for by differences in V_f. This result is perhaps not unexpected, given that Young's modulus was measured in the linear elastic region, before the onset of any irreversible behaviour. It is also indicative that the modification has not degraded the Young's modulus of the fibres themselves.

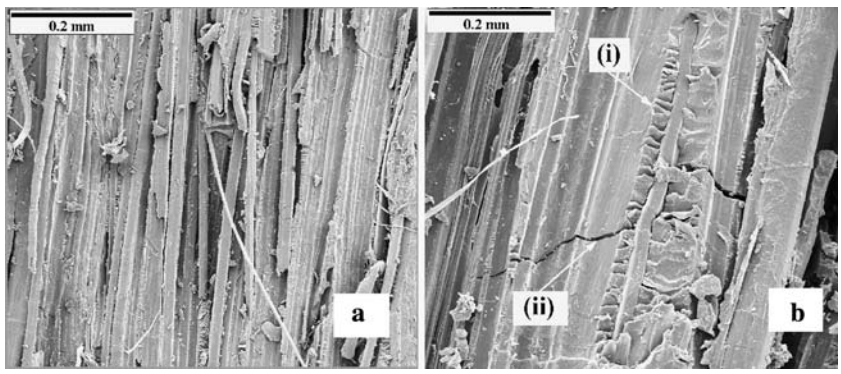

Fig. 3 SEM photomicrographs of a failed UnM flax fibre reinforced laminate. The fracture surface is parallel to the fibre axis

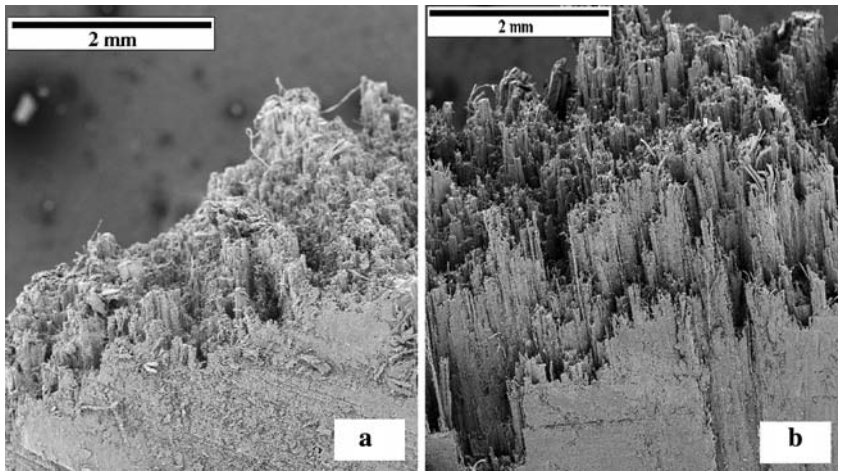

Fig. 4 SEM photomicrographs of failed MeH (**a**) and PrA (**b**) modified flax fibre reinforced laminates

What was significant about fibre modification was the effect that is had upon the tensile strength and strain to failure of the natural fibre reinforced materials. The unmodified flax fibre reinforced composites had, on average, a tensile strength of 304 MPa, with a strain to failure of some 1.73%. Modification of the fibre with propionic anhydride led to a reduction in both tensile strength (~235 MPa) and strain to failure (1.12%). With the methacrylic anhydride modified fibre reinforced materials, the reduction was even more pronounced with the average tensile strength having been reduced to 165 MPa, with a corresponding average failure strain of 0.79%. Although no experimental measurements of interfacial bond strength were undertaken in this work, differences in bond strength might be expected with the different systems. Whilst fibre–matrix adhesion would seem to have been substantially greater in the modified fibre reinforced systems, it is unclear from the fractographic evidence presented in section ''Fractography'' whether the level of fibre–matrix adhesion differed between the PrA and MeA modified fibre reinforced materials. With the PrA modified fibre, better interaction (i.e. the wet out of fibres) might have been expected due to the greater hydrophobicity introduced following modification, whereas with the MeA modified fibre reinforced material, true chemical bonding between the fibre surface and the matrix may have existed [24]. It might, therefore, be expected that the greatest interfacial bond strength would be observed in the MeA modified fibre reinforced material, with interfacial bond strength in the PrA modified fibre reinforced composite being somewhat lower. If it is assumed that the interfacial bond strength follows the trend MeA > PrA > UnM, then this might explain the observed fracture behaviour of the composites. In those composites with a strong interfacial bond, fibre–matrix debonding would be suppressed, inhibiting the ability of fibres to pullout of the matrix thereby giving rise to low strains to failure and a low work of fracture. From Fig. 6, it is clear that work of fracture (measured as the area under stress–strain curve) follows the trend UnM > PrA > MeA. This would indicate that the bond strength in the MeA modified fibre reinforced systems exceeded that of the PrA modified fibre reinforced system by some measure, and in both modified fibre reinforced systems the interfacial bond strength was greater than in the unmodified fibre reinforced system. It must, however,

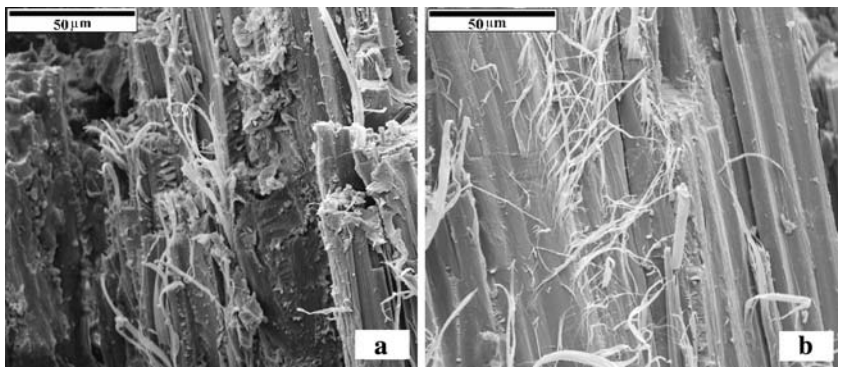

Fig. 5 SEM photomicrographs of failed MeH (**a**) and PrA (**b**) modified flax fibre reinforced laminates showing fibrillation at the fibre surface

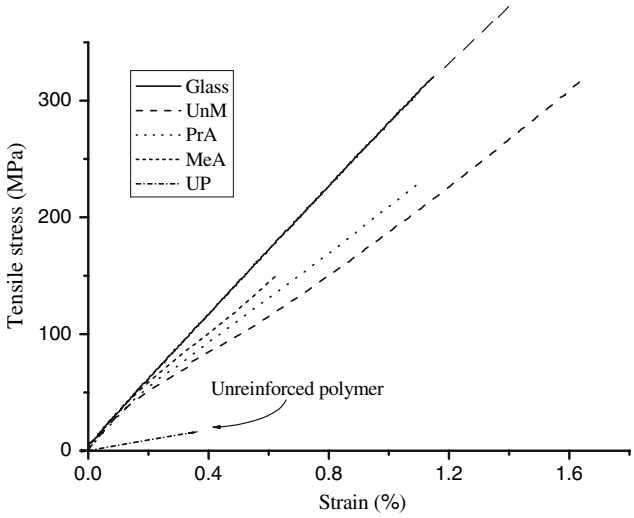

Fig. 6 Typical stress–strain curves from tensile tests performed on unreinforced polymer, glass fibre reinforced laminates and UnM, PrA and MeA flax fibre reinforced unsaturated polyester composites

be remembered that no measure of fibre properties was carried out in this study and thus a reduction in the tensile strength of the fibre following modification cannot be ruled out. This would, of course, impact upon the tensile strength of the composite.

Deformation behaviour

A typical stress–strain curve obtained from a tensile test performed on an UnM flax fibre reinforced unsaturated polyester laminate is show in Fig. 7. As may be observed, the curve is non-linear and distinct regions may be identified. The initial portion of the curve (A) is essentially linear and remains so up to an average strain of around 0.06%. At an average strain of 0.12% (B), a distinct knee in the curve, denoted by a rapid change in gradient, is observed. In the following region (C) there is a drop in the modulus initially, but then a gradual increase (D), which precedes failure at E. This behaviour is entirely different from that observed in the glass fibre reinforced material which exhibited predominantly linear behaviour to failure (see Fig. 6).

Loading to various pre-set points along the stress–strain curve prior to, and after, the knee and then unloading (Fig. 8) provided an insight into to whether the processes leading to the occurrence of the knee were reversible or not. Up to point A (Fig. 8), in the linear region of the curve before the knee, the unloading record is effectively superimposed upon the loading record, indicating that the process is reversible. Loading to a set point after the knee, point B (Fig. 8), followed by unloading, resulted in hysteresis, indicating that there was a degree of irreversibility in the process arising from microstructural damage, possibly accompanied by some non-linear elastic or viscoelastic behaviour. Once the load was removed entirely after loading to point B, a permanent deformation has been imparted to the laminate. Thus, it appears probable that at least part of the processes associated with the ''knee'' are irreversible microstructural events, leading to what might be termed a ''yield'' point. An average yield stress can be associated with this point, having a value of around 36 MPa.

The effect of varying interfacial adhesion

In composite materials, microstructural damage that gives rise to yielding can result from a number of processes, including fibre fracture, matrix yielding, matrix fracture and fibre–matrix debonding. The influence that fibre–matrix debonding has upon this behaviour was investigated by varying the degree of interfacial adhesion and by analysing and comparing the stress–strain curves of laminates reinforced with both modified and unmodified fibre. As noted in section ''Fractography'', the degree of interfacial adhesion was altered through chemical modification of the fibre and this is reflected in the modified stress–strain behaviour observed in Fig. 6. An analysis of this behaviour is presented in Table 3, below.

Individual stress–strain curves were analysed as follows: tangent moduli were constructed using Origin®

Table 2 A summary of the mechanical properties of Un-reinforced polymer, E-glass fibre, UnM, MeA and PrA modified flax fibre reinforced unsaturated polyester matrix composites

Reinforcement type	No of samples	Average V_f (%)	Laminate density (kg/m^3)	Young's modulus (GPa)	Tensile stress at break (MPa)	Strain at maximum stress (%)
Polymer	6	0	1,180 (12)	4.7 (0.1)	31 (4)	0.68 (0.12)
UnM flax	10	57.6 (2.1)	1,302 (27)	29.9 (1.8)	304 (29)	1.73 (0.10)
PrA flax	4	55.2 (2.3)	1,287 (31)	27.8 (2.3)	234 (17)	1.12 (0.05)
MeA flax	4	59.6 (4.3)	1,288 (53)	27.8 (3.1)	165 (23)	0.79 (0.15)
E-glass	4	42.4 (3.5)	1,684 (74)	30.6 (2.2)	695 (60)	2.37 (0.36)

Note: Figures in parentheses are standard deviations

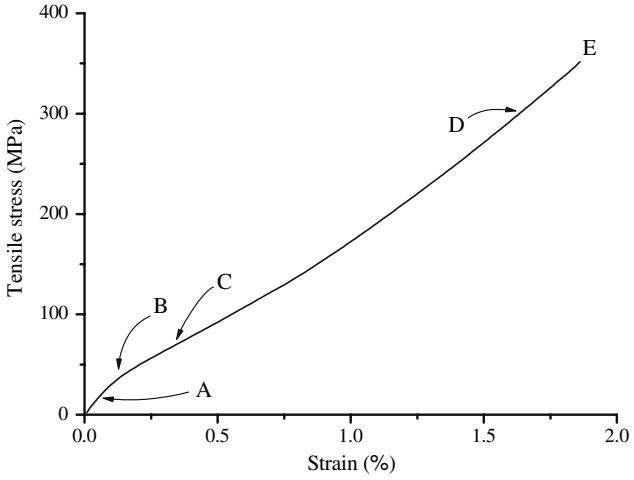

Fig. 7 A typical stress–strain curve from a tensile test performed on an UnM flax fibre reinforced unsaturated polyester composite

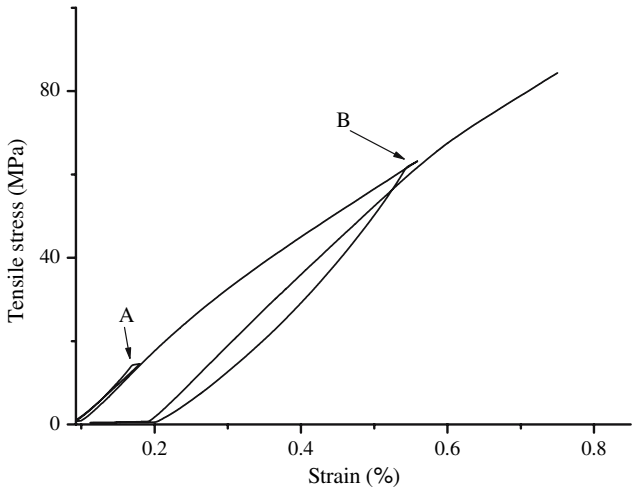

Fig. 8 Portion of loading–unloading curve (region up to failure is not shown) for a UnM fibre reinforced laminate, loaded to a point just below the yield (**a**) and after the yield point (**b**)

software, from which values of Young's modulus—E and the tangent modulus in the region immediately after the yield point (region C, Fig. 7) were computed. The intersection of these two tangents provided a value for yield strain. Yield stress was taken directly from the stress–strain curve at the yield strain. The initial departure from linearity was used to determine the onset of yielding, and values for the onset stress and strain are presented along with Young's and tangent modulii in Table 3. As may be observed, there was little difference in the average Young's modulus between the unmodified and modified fibre reinforced laminates (29.9 GPa vs. 27.8 GPa). However, following yielding, the reduction in laminate stiffness, shown as the difference between Young's modulus and the tangent modulus, was significantly less in the modified fibre reinforced laminates, indicating a change in the micromechanical behaviour. With the UnM fibre reinforced laminates the drop in stiffness after yielding was approximately 54%, whereas with both the PrA and MeA modified fibre reinforced laminates this drop-off was significantly less, being 33% and 35%, respectively. Additionally, the values for both yield stress and yield strain were greater in the modified fibre reinforced laminates. It is interesting to note that there was little difference between the two modified fibre forms in terms of the loss in laminate stiffness or the values of yield stress and strain. This would indicate that the degree of interfacial adhesion provided by these two modification types had little direct effect upon the micromechanical deformation and failure mechanisms leading to the yielding phenomenon. Whilst, as was discussed in section ''Chemical modification'', the degree of interfacial adhesion provided by these two modification regimes might be expected to differ, it is possible that some threshold value of interfacial adhesion has been exceeded with both modification methods, beyond which further improvements in adhesion are not manifested in the properties of the composite. This contention is supported by the observation that although modification does influence the onset of yielding behaviour (see Table 3), with both the PrA and MeA flax reinforced laminates showing onset values greater than the unmodified fibre reinforced material, little difference between the two modified fibre types was noted.

Acoustic emissions

In an attempt to understand the microstructural failure events contributing to the yielding behaviour of the

Table 3 Analysis of the influence of fibre–matrix adhesion upon yielding behaviour

Reinforcement type	Modulus			Yield onset		Yield point	
	Young's Modulus (GPa)	Tangent modulus (GPa)	Differ-ence (%)	Onset strain (%)	Onset Stress (MPa)	Yield strain (%)	Yield Stress (MPa)
UnM	29.9 (1.8)	13.7 (0.9)	–54	0.06 (0.01)	18.1 (3.9)	0.12 (0.01)	32.3 (2.3)
PrA	27.8 (2.3)	18.6 (2.7)	–33	0.13 (0.02)	38.2 (6.2)	0.18 (0.02)	48.4 (5.7)
MeA	27.8 (3.1)	18.1 (2.9)	–35	0.11 (0.01)	31.1 (2.8)	0.17 (0.04)	46.6 (9.8)

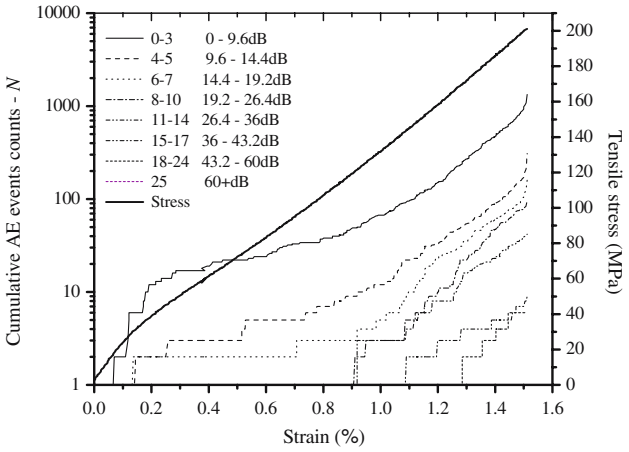

Fig. 9 Acoustic emissions from an UnM reinforced laminate, showing cumulative AE events as a function of strain, together with the corresponding stress–strain response of the laminate

laminates, acoustic emissions (AE) analysis was employed. Figure 9 shows a typical stress–strain curve for an UnM flax fibre reinforced laminate with accompanying AE emissions, presented as cumulative event counts—*N*. The system comprised 25 channels each of 2.4 dB width. To facilitate simpler analysis, the channels were grouped into 8 bands as shown in the Fig. 9. As may be observed, AE events were first recorded at strain values of less than 0.1% for channels 0–3 (0–9.6 dB) and between 0.1% and 0.2% strain for channels 4–7 (9.6–19.2 dB). Guild and co-workers [28], who used a similar system, but employing 50 channels of 1.2 dB width, found that in channels 0–3 (i.e. 0–4.8 dB) background noise was present and, therefore, excluded these from their analysis. In this work, events occurring in channels 0–3 have been included and as may be observed from Fig. 9, cumulative counts in this range rose rapidly between 0.1% and around 0.3% strain, which corresponded with the yield point. This evidence suggests that microstructural failure events did indeed occur in the vicinity of the yield point. However, from the AE analysis undertaken in this work, it was not possible to draw any firm conclusions about the exact nature of these events.

Discussion

At a fibre volume fraction of approximately 0.55, the Young's modulus, E_c, of the unidirectional modified and unmodified natural fibre reinforced composites studied in this work was in the region of 30 GPa. Applying the well known ''Rule of Mixtures'' relationship (Eq. 2) and assuming values for E_f and E_m of 76 GPa and 3 Gpa, respectively [1], a comparable glass fibre reinforced composite, of 0.55 V_f, might be expected to display a Young's modulus of around 43 GPa.

$$E_c = V_f E_f + (1 - V_f) E_m \quad (2)$$

where: E_c is the composite Young's modulus, E_f is the fibre Young's modulus, E_m is the matrix Young's modulus.

Whilst the absolute value of E_c for the man made fibre reinforced composite is greater, when the lower density of the natural fibre reinforced material is taken into account, the specific stiffness values are comparable. Where stiffness is the main design criterion, therefore, natural fibre reinforced composites offer good promise in structural or semi-structural applications. However, whilst the initial stiffness of the laminates is of value in engineering terms, the existence of a distinct yield point may well have a significant impact in practice.

Both the modified and unmodified natural fibre reinforced polymer matrix composites laminates studied in this work revealed a departure from linear behaviour at low values of stress and strain when the materials were loaded in tension parallel to the direction of the fibre (see Table 3). This behaviour was entirely different from that observed in either the unreinforced polymer or the unidirectional glass fibre reinforced laminates, both of which exhibited ostensibly linear behaviour to the point of fracture (see Fig. 6). It seems highly probable that this departure from linearity is associated with a true ''yield point'', since once the laminates were loaded to beyond the yield point and then unloaded, they were found to have undergone permanent deformation (see Fig. 8). It is interesting to note the similarity between this behaviour and the yielding observed in cross-ply laminates, wherein yielding results from failure in the transverse plies [30]. Whilst in the materials considered in this work, yielding cannot be associated with off-axis plies, it must, nevertheless, result from some form of irreversible microstructural damage. This contention is supported by the AE analysis where acoustic events (admittedly of low audibility and low frequency) were first detected in the region of the yield point, indicating incipient microstructural damage.

To look for the origins of this behaviour it is first necessary to consider the characteristics of the reinforcing fibres themselves as well as the interaction between the fibre and the matrix. Unlike glass fibres, which are essentially homogeneous and display linear elastic behaviour to failure, flax fibres are not only

heterogeneous in structure, but they can also display non-linear deformation behaviour. Hornsby and co-workers [31], for example, observed strain hardening in flax fibres subject to tensile loading, whilst Baley [32] also reported non-linear characteristics, ascribing this behaviour in flax to the ''extension of defects'' and ''reorganisation of the cellulose fibrils in the direction of the fibre axis''. It is well known that flax fibres possess microstructural defects, known variously as ''nodes'', ''slip planes'' or ''kink bands'' (see Fig. 10) and that the presence of such features results in a reduction in both the tensile strength and Young's modulus of the fibres [9]. Furthermore, it is known that these defects directly contribute to the non-linear straining behaviour of flax fibres [32], which can be likened to the tensile behaviour of polymer fibres that have previously undergone compressive kinking [33]. A manifestation of these defects, when the fibres are used as composite reinforcement, is that they lead to stress concentrations in the matrix in the vicinity of the defects when the composite is loaded parallel to the axis of the fibre [20, 27].

As may be seen from Fig. 10, significant kink bands (A) occur with relative frequency along the length of a typical flax fibre, with perhaps fewer than 10 fibre diameters between successive defects [27]. These kinks may be thought of as regions of relatively lower stiffness, since when the fibres are initially strained, the defects begin to extend [32]. This supposition is supported by experimental evidence that shows strain concentrations at the defects in flax fibres when they are used in single fibre composites [18]. Furthermore, it has been shown that the Young's modulus of flax is dependent upon the ratio of damaged to defect free fibre; a greater proportion of fibre damage leading to reduced fibre stiffness [9]. Thus, by adopting a force balance approach, the net effect of this lower fibre stiffness at the defects would be the aforementioned stress concentrations in the matrix in the vicinity of the defects [27].

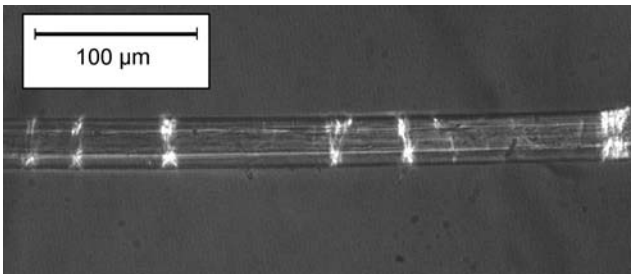

Fig. 10 Kinking in flax, shown as white bands traversing the fibre when viewed under polarised light, with crossed polarisers

Therefore, whilst the fibres themselves are continuous, the presence of kink bands along the length of the fibre would have the effect of ''segmenting'' the fibre. In this way the whole fibre could be thought to consist of a series of, typically, low aspect ratio but relatively stiff, ''segments'', ''joined'' by regions of more compliant fibre forming the kink bands. In other words, although the fibres are continuous, they may be considered to act, in part, as a series of short fibres. This is shown schematically in Fig. 11. The interfacial shear stress (τ_i), may then be expected to varying along the length of the fibre in a ''Cox-type'' shear lag manner [34]. This phenomenon has been verified experimentally elsewhere [35].

The presence of a distinct yield point in the unidirectional modified and unmodified natural fibre reinforced composites studied in this work may be explained in terms of the fibre kink bands and the consequent effect that they have upon fibre deformation behaviour. Assuming that at low values of applied strain, before the yield point, the system is elastic with elastic stress transfer taking place over each of the fibre segments following a ''Cox-type'' shear-lag mechanism, the greatest values of τ_i would occur at the ends of each of the fibre segments (it will be recalled that the segments are bounded by kink bands). As the strain applied to the composite increases, τ_i will increase at the fibre ends until its magnitude reaches some maximum, or critical value, τ_{i*}, at which debonding begins. Indeed, high local interfacial shear stresses at the segment ends may also be exacerbated by the distinct geometry of the defects [20]. In addition to breakdown of the interface resulting from interfacial shear stresses at the segment ends, the localised stress concentrations in the vicinity of the kink bands may also lead to failure of the matrix [20]. However, it seems highly probable that fibre–matrix debonding contributes substantially to the yielding phenomenon, since modifying the fibres to improve adhesion between the two phases has a marked effect upon the yield point.

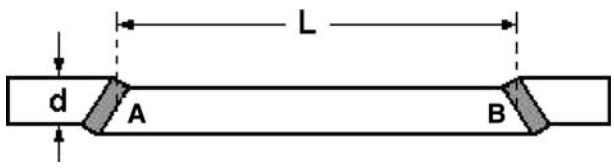

Fig. 11 Schematic representation of a fibre segment bounded by damage in the form of kink bands at A and B. The aspect ratio of the segment, s, is defined as the segment length, L, divided by the fibre diameter, d

With both the PrA and MeA modified fibre reinforced composites, the yield stress increases to around 46–48 MPa, from around 32 MPa for the UnM fibre reinforced material. The corresponding yield strain increases from 0.12% for the UnM modified fibre reinforced composites to around 0.18% for the PrA and MeA modified fibre reinforced materials. Such an increase would be expected if the value of the maximum interfacial shear stress, τ_{i*}, were greater, thereby suppressing the onset of fibre–matrix debonding. This would also explain why the drop-off in modulus is less with the modified fibre reinforced composites; the reinforcing efficacy of the fibre segments would be retained since a greater proportion of stress transfer would take place through elastic processes rather than by slip, following interface breakdown. Nevertheless, some inelastic processes must be operative to give rise to macroscopic yielding behaviour. It is interesting to note that there is little difference in either the yield point or the onset of yielding between the two modified fibre types, even though differences in the level of adhesion might be expected. Nevertheless, as will be discussed in more detail later in this section, the level of adhesion may well be a significant factor during fracture.

The contention that natural fibres act in the manner of a series of short, stiff, fibres or ''segments'', joined together by regions of relatively lower stiffness fibre can be reasoned in an alternative fashion. Firstly, it is assumed that flax fibres are homogeneous and that they behave as Hookean materials. Then, by applying the well known ''Rules of Mixtures'' relationship (Eq. 2) for composites with continuous fibres and substituting for the experimentally derived values of; V_f (0.58), E_c (29.9 GPa) and E_m (4.7 GPa), for the UnM fibre reinforced composite, the Young's modulus of the fibre would be approximately 48 GPa.

However, the average post yielding tangent modulus of the UnM fibre reinforced composite is 13.7 GPa which is approximately half the value of E_c. Since the applied strain at yield onset (0.06%) is significantly lower than the expected failure strain of the fibres (1–3%) little or no fibre failure would be anticipated as yielding begins. Assuming then that there was no fibre fracture, even if there were to be no further contribution to the composite stiffness from the matrix following yielding, the theoretical stiffness of the composite would still be in the region of 28 GPa from the contribution made by the fibres alone. This is clearly not the case, since the modulus immediately after the yield point is only 13.7 GPa.

If, instead, it is assumed that the fibre acts as a series of segments which individually behave in a linear-elastic manner, embedded in a matrix which itself is assumed to be linear-elastic, it is possible to describe the deformation behaviour of the composite using a Cox-type shear lag model. Equation 3 [1] expresses the theoretical elastic stress–strain relationship before the onset of yielding.

$$\sigma_1 = \varepsilon_1 \left[V_f E_{fs} \left(1 - \frac{\tanh(ns)}{ns} \right) + (1 - V_f) E_m \right] \tag{3}$$

Where n is given by:

$$n = \left[\frac{2E_m}{E_{fs}(1 + \nu_m)\ln(1/V_f)} \right]^{1/2}$$

and where: σ_1 is the composite tensile stress, ε_1 is the composite tensile strain, ν_m is the matrix Poisson's ratio and assumed to be 0.35 [1], E_{fs} is the Young's modulus of the fibre segment.

Assuming that E_{fs} is the same as the stiffness of the fibre free from defects, or fibre having had all defects ''pulled-out'', and is taken to be 90 GPa [9, 32], it is possible to construct theoretical stress–strain curves for different values of s, the segment aspect ratio.

Figure 12 shows for a range of values of s, the theoretical stress–strain curves in the region before yield onset. As the value of s increases, the derived composite modulus increases and reaches a maximum value as $s \rightarrow \infty$. What is of significance, however, is that as s decreases to values that might be expected to represent segments in real fibres, around $s = 5$, the derived theoretical composite Young's modulus of 28 GPa approximates the experimental values obtained in this work. Many assumptions and simplifications have necessarily been made in this analysis—in particular it

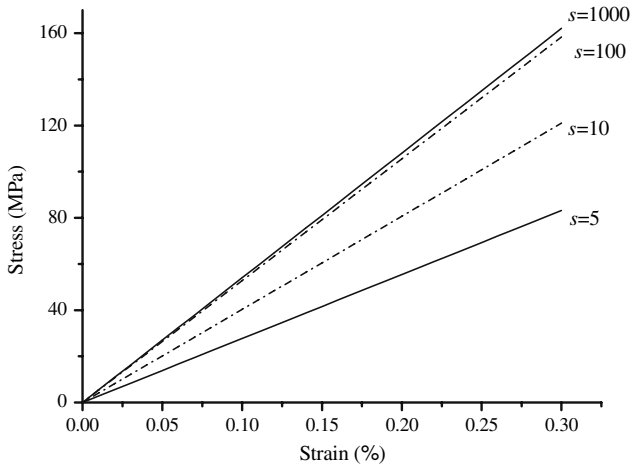

Fig. 12 Theoretical stress–strain curves in the region before the yield point, for a range of values of s

has been assumed that the fibres are discontinuous and the effect of the defects (kink bands) themselves has been disregarded—however, the analysis does serve to show that the model is physically realistic.

Following the same approach, it is possible to predict the onset of inelastic composite behaviour. Equation 4 provides an expression for the composite strain at the onset of interfacial sliding (ε_{1*}), which is assumed to occur when the interfacial shear stress reaches a maximum value (τ_{i*}) where debonding takes place.

$$\varepsilon_{1^*} = \frac{2\tau_{i^*}\coth(ns)}{nE_f} \tag{4}$$

For the UnM fibre reinforced composite, assuming s to be equal to 5 and the onset of yield to occur at a composite strain of 0.06%, a value for τ_{i*}, of around 9.7 MPa is predicted. There are few values for τ_{i*} reported in the literature for natural fibre composite systems and those that have been reported, vary widely. Hill and Abdul Khalil [36], for example, reported values of between 1.5 MPa and 2.0 MPa for the maximum interfacial shear stress of modified and unmodified oil palm and coir fibre reinforced unsaturated polyester composites. Recently, Eichhorn and Young [19], using a micro-droplet technique combined with Raman spectroscopy, found that the maximum interfacial shear stress in single hemp fibre-epoxy composites was ''of the order of the shear yield stress of the resin (40–45 MPa)''. Other workers have, for instance, obtained intermediate values depending upon the composite system and the experimental method employed [37]. A value of 9.7 MPa is, therefore, consistent with what might be physically reasonable for such a system.

The relationship also predicts that as τ_{i*} increases so too does the onset of yield (ε_{i*}). Clearly, there is a difference in the onset point between the modified and unmodified fibre types, however, as discussed previously, there appears to be a threshold value of τ_{i*}, above which no change in the onset of yielding or the yield point itself is observed. This is evidenced by the observation that neither the onset of yielding nor the yield point itself differs significantly between the PrA and MeA modified fibre reinforced composites. Since a difference would be expected from the type of bonding formed between fibre and matrix, this may indicate that other microstructural failure processes, such as matrix failure become dominant as interfacial adhesion is improved.

Beyond the yield point, the initial drop-off in the laminate stiffness (region C in Fig. 7) is explained by the occurrence of microstructural damage as discussed above. As loading continues, however, the stiffness of the UnM fibre reinforced laminate appears to increase again (region D in Fig. 7). It is probable that this phenomenon arises from the non-linear, ''strain hardening'' behaviour of the reinforcing fibres themselves. Microstructural damage in the form of fibre–matrix debonding and matrix failure, occurring in region C, in the vicinity of the yield point would partially liberate the fibres from the encapsulating matrix, allowing them to ''realign''. This realignment most probably takes the form of an ''extension of the defects'' [32] in the first instance that would tend to increase stiffness and would be manifested in the composite as an increase in modulus. It seems probable that during fabrication, initially kinked fibres would either undergo further kink band formation or that existing damage would be exacerbated. The matrix used in this work was an unsaturated polyester resin and it is well known that these polymers undergo significant volumetric shrinkage during curing, which might be expected to place the reinforcing fibres under compression, resulting in kink band formation. This phenomenon is observed in synthetic polymer fibres when processed into composites [38]. Cure shrinkage and its effects upon the reinforcing fibres might be expected to exacerbate the effects of the non-linear behaviour observed in these materials.

The influence of fibre modification is perhaps most noticeable in its effect upon the failure of the laminates. With the modified fibre reinforced laminates, a significant reduction in tensile strength is observed. In these composites a strong interfacial bond might be expected, leading to suppression of fibre–matrix debonding. This would tend to inhibit the ability of fibres to pullout from the matrix thereby giving rise to low strains to failure and a low work of fracture. It is, perhaps, significant that the failure strain of the MeA modified fibre reinforced laminates, at an average of 0.79%, is lower than the failure strain that might be expected from the fibre and is of the same order as that of the resin. The average failure strain of the PrA modified fibre reinforced material is somewhat greater, at 1.12%, which might indicate that the microstructural failure mechanisms differ between the two modified fibre reinforced composite systems. Clearly, modification may well affect the strength of the fibre and, as this has not been verified separately in this work, it is inappropriate to draw firm conclusions regarding the ultimate failure of the composites. Nevertheless, if the interaction between the two modified fibre types and the matrix is considered further, it might be expected that under mode II interfacial loading, failure would be dominated not only by the fibre–matrix adhesion, but also by the surface roughness of the fibres resulting from the

numerous kink bands. Under mode I interfacial loading, however, it is to be expected that failure would be dominated by the adhesion between the two phases. In other words the chemical bond between the MeA fibre and matrix might be expected to suppress crack opening under mode I conditions, and might thus be expected to inhibit Cook–Gordon type crack blunting mechanisms [39], thereby leading to lower strains to failure.

Conclusions

The work reported herein has demonstrated that whilst in terms of Young's modulus, flax fibre reinforced unsaturated polyester resin composites can compete favourably with their glass fibre equivalents, they deform in a non-linear fashion. Examination of the stress–strain curves and acoustic emissions analysis has provided strong evidence that these materials undergo yielding at comparatively low values of stress and strain. It seems highly probable that this yielding behaviour arises as result of the non-linear deformation behaviour of the flax reinforcing fibres caused by the presence of kink bands and also the effect that these defects have upon the stress transfer.

Whilst many assumptions have, necessarily, been made in the theoretical analysis applied to this behaviour, the effects are real and will have practical implications for the use of these materials in structural applications. Further work is ongoing to elucidate the microstructural processes involved in the expectance that a fuller understanding of this behaviour, and methods by which it may be overcome, will be developed.

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