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Compressive behaviour of unidirectional flax fibre reinforced composites

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The compressive strength of unidirectional flax fibre epoxy composites was studied. The compressive strength is influenced negatively by the presence of kink bands in the flax fibres. Improvement of the adhesion between the fibres and the epoxy resin can be achieved easily by removing the thin wax layer which covers the surface of the flax fibres. However, improving the adhesion between fibres and matrix only improves the compressive strength to a very limited extent. Stabilisation of the kink bands present in the fibres and improvement of the compressive properties of the fibres can be achieved by impregnating the fibres with melamine formaldehyde (MF) resin. This results in a large increase in the compressive strength of the resulting composite. The increase in compressive strength is proportional to the amount of MF resin present in the composite. However, the presence of the resin in the fibres lowers their tensile strength, and subsequently the tensile strength of the resulting composite.

1. Introduction

Annual fibre reinforced composites receive an ever increasing attention due to their potentially very good properties. Fibres like hemp and jute but especially flax have intrinsic properties which come close to the properties of glass fibres (see Table I for a comparison between flax fibres and glass fibres) [1, 2]. Some materials in which the fibres are combined with polyolefins, like polypropylene (PP), are already commercially available [3]. In all these materials the annual fibres are present as short fibres with lengths ranging from circa one millimetre to a few centimetres or as randomly oriented fibre non-wovens.

Composites with long fibre reinforcement, like unidirectional (UD) composites, are up to now not commercially produced from annual fibres. Apart from the experimental problems in producing these kind of materials, the application of unidirectional annual fibre reinforced composites is also hampered by their relatively poor compressive properties [4].

The compressive properties of the fibres are influenced by the fibre structure and by the decortication process which is commonly used to isolate the fibres from the plants. The structure of the fibre is composite-like by itself [5]. A schematic structure of the flax fibre, from stem to microfibril, is given in Fig. 1. The coarse bast fibre bundles that grow in the plant stem are isolated from the stem by breaking (breaking the wooden core of the stem by bending it) and scutching (beating the wooden particles out of the fibre bundles) and further refined towards technical fibres by hackling (combing). The technical fibres consist of elementary fibres. The elementary fibres have lengths between 2 and 5 cm, and diameters between 10 and 25 μm. The technical fibre consists of about 10–40 elementary fibres in cross section. The elementary fibres overlap over a considerable length. They are not circular but a polyhedron with usually 5, 6 or 7 angles to improve the packing in the technical fibre. The elementary fibres are the single plant cells. They consist of a primary cell wall (not shown in Fig. 1), a secondary cell wall and a lumen, which is an open channel in the centre of the fibre. The lumen can be as small as 1.5% of the cross section [6]. Elementary fibres contain 65–75% cellulose, circa 15% hemicellulose (mostly xylan) and 10–15% pectin [7, 8]. The pectin is mainly situated in the primary cell wall [9–11], which further contains some lignin and (hemi)cellulose [10, 11]. The primary cell wall is relatively thin, in the order of 0.2 μm [12]. The fibres also contain 2–5% of waxes [13], part of which can be found on the surface of the primary cell wall. The waxes might originate from the plant cuticle, which is made up of cutin, an aliphatic polyester, embedded in soluble waxes, mainly palmitic acid [14–16]. Van de Velde and Kiekens [17] find a contact angle of scutched dew retted flax fibres in water of circa 70–80°, indicating that the fibres are partly wetted out by water, and consequently that the fibre surface is rather hydrophilic. Van Hazendonk *et al*. [18] on the other hand studied the surface tension of flax fibres which have undergone various

TABLE I Glass fibre and flax fibre properties compared

Property	E-glass [1]	Flax fibres [2]
Diameter (μm)	8–14	10–80
Density (g/cm^3)	2.56	1.4
E-modulus (GPa)	76	50–70
Tensile strength (GPa)	1.4–2.5	0.5–1.5
Elongation to fracture (%)	1.8–3.2	2–3
Specific E-modulus (GPa per g/cm^3)	30	36–50
Specific tensile strength (GPa per g/cm^3)	0.5–1	0.4–1.1

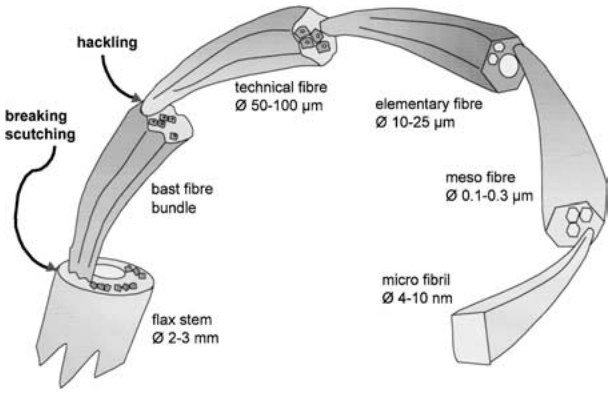


Figure 1 Schematic representation of flax fibre built-up.

surface treatments to remove the subsequent outer layers. They find that the surface tension of retted flax fibres is very low (γ_s = 28.5–34.2 m Nm^{-1}), and comparable to the surface tension of waxes. Extraction of the fatty substances makes the fibre more hydrophilic and increases the surface tension (γ_s = 40.3–43.1 m Nm^{-1}). Additional extraction of pectins and hemicelluloses further raises the surface tension to a value comparable to that of highly crystalline cellulose (γ_s = 60.5–66.1 m Nm^{-1}). The secondary cell wall makes up most of the fibre diameter, and is made mainly from cellulose and hemicelluloses [13]. The cellulose is laid down in oriented, highly crystalline microfibrils glued together by the amorphous hemicellulose phase. The hemicellulose is known to contribute significantly to the strength of the fibre, removal of the hemicellulose results in a dramatically reduced tensile strength, and causes the fibre bundles to completely disintegrate into microfibrils [9, 19]. Astley and Donald [20] studied the flax cell wall with small-angle X-ray scattering (SAXS) and derived from the data analysis that the cross section of the cellulose microfibrils is circa 10×50 Å^2. Näslund *et al*. [21] report a microfibril diameter between 1 and 4 nm, as measured by diffraction contrast transmission electron microscopy. Astley and Donald [20] also find evidence for a crystalline/non-crystalline repeat distance of 60–70 Å. The microfibrils are packed together in a fibrillar structure, the meso fibrils, with a fibril size in the order of 0.1 to 0.3 μm. The fibrils are oriented spirally at approximately $+10^\circ$ compared to the fibre axis [22].

The highly oriented crystalline structure of the secondary cell wall makes the fibres sensitive to kink band formation under compression (see Fig. 2). The standard processes by which the fibres are presently isolated from the plants—breaking, scutching and hackling-involve a lot of bending of the fibres to remove the wooden core of the plant and consequently introduce kink bands in the fibre structure which negatively influence the compressive strength of the fibres [5]. The meso fibre structure inside the kink bands is known to be seriously distorted after these isolation procedures [2, 5]. Due to the bending of the cell walls the lateral bond between the fibrils in the cell wall is locally destroyed and the fibrils are separated, leaving a structure which resembles a crack, bridged at equal distances by cellulose fibrils [5]. This structure is not expected to be able to withstand compressive loading, and this is probably one reason for the poor compressive behaviour of unidirectional flax fibre composites.

This paper investigates options to improve the compressive properties of unidirectional reinforced flax fibre-epoxy composites. In order to improve the compressive properties of UD flax fibre reinforced epoxy composites, both the adhesion between fibre and matrix and the stabilisation of kink bands were addressed.

As discussed above, the surface of flax fibres is by nature covered with a thin layer of waxes, which might strongly reduce the accessibility of the reactive hydroxyl groups of the pectin and cellulose components on the fibre surface. Removing the wax layer will then increase the reactivity of the fibre surface towards various substances.

Epoxies can normally easily react with hydroxyl groups. However, reaction of the hydroxyl groups on the fibre surface with the epoxy resin might be hampered by there spatial postitions. Many of the hydroxyl groups in the cellulose crystals are known to form inter- and intracrystalline hydrogen bridges [23] which reduces their reactivity. Furthermore, a large part of the accessible hydroxyl groups are probably located on the pectins and hemicelluloses, and the strength of the adhesion between the pectins and hemicelluloses and the cellulose crystals is unknown.

To improve the reactivity of the fibres towards the resin a modification step with maleic anhydride (MA) can be carried out. Maleic anhydride is known to be reactive towards the surface of cellulose fibres [24]. This fact is frequently used in the compatibilisation of flax/PP composites, where maleic anhydride modified PP can be very effective to improve composite strength and impact behaviour [25]. At elevated temperatures, maleic anhydride can form an ester bond with a hydroxyl group of the fibre surface [26], creating a free hydroxyl group protruding from the surface which is better accessible than the surface hydroxyl groups and which can subsequently react with the epoxy resin. Therefore, maleic anhydride is expected to increase the adhesion between fibres and matrix, but it is not expected to stabilise the kink bands present in the flax fibre structure.

In order to stabilise the kink bands in the fibres, a component would be needed that is actually able to penetrate into the fibre and fill the holes between the fibrils in the kink band. It is known from work done by Rapp *et al*. [27] that modified melamine formaldehyde resin is able to penetrate into the cell wall of a

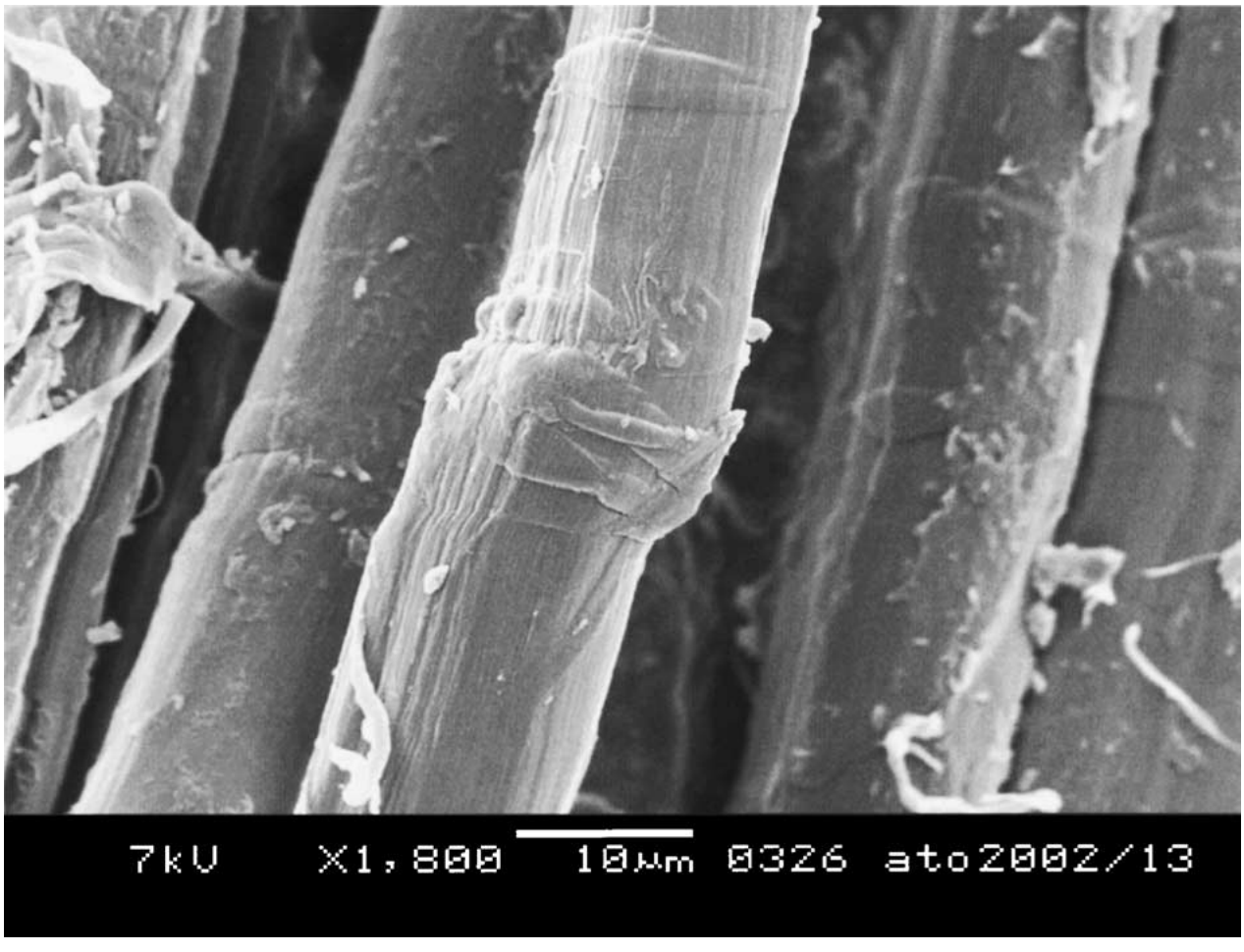


Figure 2 Kink bands in a flax fibre, scale bar represents 10 μm.

number of wood species. It is therefore not unlikely that melamine formaldehyde (MF) resin is also able to penetrate into the cell wall of flax fibres. Rapp *et al*. show that concentration of melamine resin in the cell wall of *Picea abies* Karst. sapwood can become as high as 20 to 30% after soaking in a watery resin solution. High values like these would in the case of flax fibres certainly be sufficient to fill the hole-like defects in the kink bands and stabilise the fibres under compression. Furthermore it is possible that the melamine resin not only fills the holes in the cell wall but also diffuses in between and into the cellulose fibrils in the secondary cell wall and so internally crosslinks the fibre, forming covalent bonds in and between the fibrils.

2. Experimental

2.1. Materials

Flax (JS-33-1995, Cebeco, NL) was warm water retted on pilot scale and decorticated via breaking, scutching and hackling.

Glass was standard E-glass roving with epoxy sizing, kindly supplied by Aerpac.

Standard viscose 'Cudenka 700 yarn' was kindly supplied by AKZO-NOBEL. This yarn contains a twist.

Epoxy Ampreg 20 from SP Systems with ultra-slow harder, 100:30 (w/w) was kindly supplied by Aerpac.

Maleic anhydride (MA) was purchased from Merck.

MF resin Madurit MW909 was kindly supplied by DSM.

2.2. Methods

Dewaxing was performed via an extraction in duplo using boiling ethanol during 3 h, a method which is known to remove the waxy substances but not the pectins from the surface [18].

Modification with MA was performed in the gas phase. MA was heated up to 100°C and flax fibres were held in the MA vapour during one hour. During this process the MA sublimates on the fibre and reacts with the available hydroxyl groups. The modified fibres were dried during 2 days at 50°C during which the non-reacted MA evaporates [28]. The percentage of MA on the fibres was determined by saponification and subsequent HPLC and was found to be 0.29 wt%.

Treatment of the fibres with epoxy resin or MF was performed according to the following procedure: epoxy resin was dissolved in methanol, MF was dissolved in water. The flax bundles were soaked in the solution during 10 min at room temperature and dried overnight at 70°C. The percentage resin on the fibres was determined by weighing. To investigate the influence of the treatment procedure the standard treatment was adjusted: the time of soaking the fibres in the MF solution was varied to 5 min and to 1 h; the temperature

at which the fibres were impregnated was increased to 70°C; some of the fibres were pre-swelled in water during 3 h to make them more accessible to the MF solution.

2.3. Sample preparation

UD composite samples were prepared via pultrusion on a lab scale set-up. The fibres were cut to the appropriate length and bundles of the desired weight were prepared. The bundles were soaked in the epoxy resin and pulled into the pultrusion mould. The samples were precured overnight at 35°C and subsequently cured overnight at 70°C.

Samples for Inter Laminar Shear Strength (ILSS) and compression tests contain 50 wt% of fibre, samples for tensile tests contain 30 wt% of fibre.

Samples for the determination of the compressive strength of the pure epoxy resin were made by pouring the fluid resin in the pultrusion mould which was closed on the bottom by a rubber stopper. The same curing cycle was used as for the pultruded composites.

2.4. Material testing

Compressive strength tests were performed on cylindrical samples with a length of 25 mm and a diameter of 6 mm, following ISO 3597-3:1993(E) at a testing speed of 1 mm/min. At least four samples were tested per material. The fibres were oriented in the length direction. The tests were performed on a Zwick 1445 universal tester. The modulus in compression was measured on samples of length 30 mm and diameter 6 mm, using three strain gauges for each sample, applied in length direction at 0°, 120° and 240°. The values are only indicative since only 1 sample was tested. The tests were performed on a 100 kN Schenk universal testing machine. The samples are longer than the compressive strength samples to fit with the strain gauges in the testing machine. Inter laminar shear strength (ILSS) values were determined on samples with dimensions $25 \times 10 \times 4$ mm^3 following ISO 4585: 1989(E), at a span length of 20 mm and a testing speed of 1 mm/min on a Zwick 1445 universal tester. At least three samples were tested. Fibre bundle strength was measured in tenfold using a stelometer (Spinlab AG) following ISO 3060 (1974) with a clamp length of 3.2 mm, a procedure which is known to yield data relevant to the fracture behaviour of flax fibres in composite materials [2]. The bundle strength of the MF impregnated fibres was measured in fivefold, following the same procedure. Tensile tests were performed in fivefold on samples of $150 \times 10 \times 2$ mm^3 at a testing speed of 1 mm/min (E-modulus) and 10 mm/min (tensile strength) following ISO R527-3: 1994. To prevent failure in the clamps, aluminium tabs were glued onto the samples with epoxy glue (Araldite). SEM micrographs were made on a Jeol JSM-5600LV scanning electron microscope. EDAX measurements were performed on a Cambridge Instruments Stereoscan 240 with a digital detector from Princeton Gamma-Tech with EDAX.

TABLE II Tensile strength ($\sigma_{tensile}$) and tensile modulus ($E_{tensile}$) of the three different fibres and ILSS, compressive strength (σ_{comp}) and compressive modulus (E_{comp}) of unmodified composites

	$\sigma_{tensile}$ (MPa)	$E_{tensile}$ (GPa)	ILSS (MPa)	σ_{comp} (MPa)	E_{comp} (GPa)
Flax	911 (192)	50[b]			
Viscose	770[a]				
Glass	2600[a]	73[a]			
Flax/epoxy			15.4 (0.4)	119 (2)	30[c]
Viscose/epoxy			39.6 (0.6)		
Glass/epoxy			65.4 (2.2)	595 (81)	33[c]

[a]Values according to the specifications of the producer.
[b]From Reference [2].
[c]Indicative values since only one sample was tested, see also reference [29].

3. Results and discussion

Table II lists the properties of the fibres and the results of compression tests and interlaminar shear strength (ILSS) tests of samples containing 50 wt% of fibres, which have not undergone any surface modification (the values between the brackets are the standard deviations). Apart from glass fibres also viscose yarn is taken as a reference material, since viscose consists almost completely of cellulose and therefore is expected to have similar reactive surface groups as flax fibres.

The interlaminar shear strength is taken as a measure for the adhesion between fibres and matrix.

It is clear from Table II that the compressive strength of the flax samples is rather low, only slightly higher than the compressive strength of the epoxy resin itself, which was found to be 82 ± 7 MPa. The compressive strength of the flax filled composites is only 20% of that of the glass filled materials.

On the other hand, it can be seen that the compressive stiffness of both the glass filled and the flax filled epoxy is similar and moreover, is in the range of what can be expected on the basis of the rule of mixtures [29].

The ILSS value of the flax composite is only 25% of that of the glass composite whereas the ILSS of the viscose composite is ca. 2.5 times as high as the ILSS of the flax composite.

The good compressive modulus of the flax epoxy composites indicates that at small strains the presence of the kink bands does not yet interfere strongly with the deformation process. The flax composites show a compressive stiffness according to the expectation. This indicates that if stabilisation of the kink bands is possible, it might be possible to produce materials with interesting properties. These results are in contrast to the results of Lamy and Pomel [30], who find a very low modulus in bending for UD flax epoxy composites and who show that this is due to the presence of kink bands and other fibre defects.

Comparison of the ILSS of the viscose and the flax composite suggests that without removal of the wax layer, good adhesion between the fibres and epoxy is not automatically achieved, and thus that flax fibres might not readily react with the epoxy resin.

Table III shows the effect of various fibre modifications on the ILSS and compressive strength of flax- and viscose epoxy composites.

TABLE III ILSS and compressive strength of flax and viscose fibre/epoxy composites with different surface modifications

	ILSS (MPa)		σ_{comp} (MPa)	
Modification	Flax	Viscose	Flax	Viscose
None	15.4 (0.4)	39.6 (0.6)	119 (2)	
Dewaxing	25.4 (0.5)	37.8 (0.9)	137 (13)	151 (5)
MA	16.7 (1.0)		141 (13)	142 (8)
Dewaxing + MA	26.7 (0.5)	42.1 (2.2)	133 (13)	
Epoxy	13.6 (0.7)	40.8 (1.6)		

Removal of the wax layer by ethanol extraction leads for flax composites to a large increase in the ILSS, and thus in the adhesion between the fibres and the matrix. As expected ethanol extraction has no significant effect on the ILSS of the viscose composite.

Modification of the surface of flax with maleic anhydride (MA) without removal of the wax layer does not significantly increase the ILSS of the flax composite (see Table III). The wax layer apparently also prevents reaction of the hydroxyl groups on the fibre surface with a small molecule like MA. Also pretreating the fibres with a solution of epoxy does not lead to additional adhesion as long as the wax layer is present. Removal of the wax layer and subsequent modification of the surface with MA leads to an ILSS value of 26.7 MPa, which is similar to the ILSS value found for flax composites which have only the wax layer removed and are reacted directly with the epoxy resin. Apparently, contrary to the assumption, once the wax layer is removed, the surface of the flax fibres is sufficiently reactive towards the epoxy resin and does not benefit additionally by the introduction of a reactive group like MA. The same effect is seen for the viscose composite, modification with MA does not lead to a significant increase in the ILSS.

These results are similar to the results of van de Velde and Kiekens [31], who report an increase in the ILSS in a UD flax PP system from circa 10 MPa to circa 24 MPa upon the addition of a compatibiliser, in this case maleic anhydride modified PP.

The influence of the surface modifications on the compressive strength of flax composites does not follow the same trends as the ILSS (see Table III). All three treatments, dewaxing, MA modification and dewaxing combined with MA modification, lead to a small increase in compressive strength of the composite. It is not clear why the MA modification, which does not influence the ILSS, does result in a composite with a slightly higher compressive strength. It is, however, obvious that the increase acquired in adhesion between the flax fibres and the matrix with the other two treatments, has only a limited effect on the strength of the composite in composite in compression.

For the viscose composite, modification with MA does not lead to a higher compressive strength.

Table IV shows the effect of the modification of the fibres with MF resin on the ILSS and the compressive strength of flax- and viscose epoxy composites. Also the influence of the concentration of the MF resin solution used for the impregnation is shown.

TABLE IV ILSS and compressive strength at different MF concentrations

Fibre	Concentration MF solution (%)	ILSS (MPa)	σ_{comp} (MPa)
Flax	10	19.7 (0.8)	
Dewaxed flax	10	30.5 (0.7)	250 (13)
	20	27.9 (0.7)	307 (21)
Viscose	10	39.5 (1.6)	220 (14)
	20	33.7 (0.4)	289 (9)

It is clear that application of MF resin (10% solution) on the flax fibres slightly increases the ILSS from 15.4 ± 0.4 MPa to 19.7 ± 0.8 MPa, even though the wax layer has not been removed. The combination of dewaxing and MF application leads to an increase of the ILSS to 30.5±0.7 MPa, which is double the value found for uncompatibilised systems. Obviously, MF increases the adhesion in flax epoxy composites to a large extent. Again, the modification has no effect on the ILSS in the viscose composites.

Applying MF resin to dewaxed flax fibres more than doubles the compressive strength of the flax composite towards a value of 250 ± 13 MPa. It is interesting to note that the compressive strength of the flax fibre reinforced composites is now higher than that of the viscose reinforced composite even through the viscose composite shows a higher ILSS value.

It is clear from these results that application of the MF resin leads to an additional effect above just the improvement of adhesion. Fig. 3 shows two SEM-EDAX

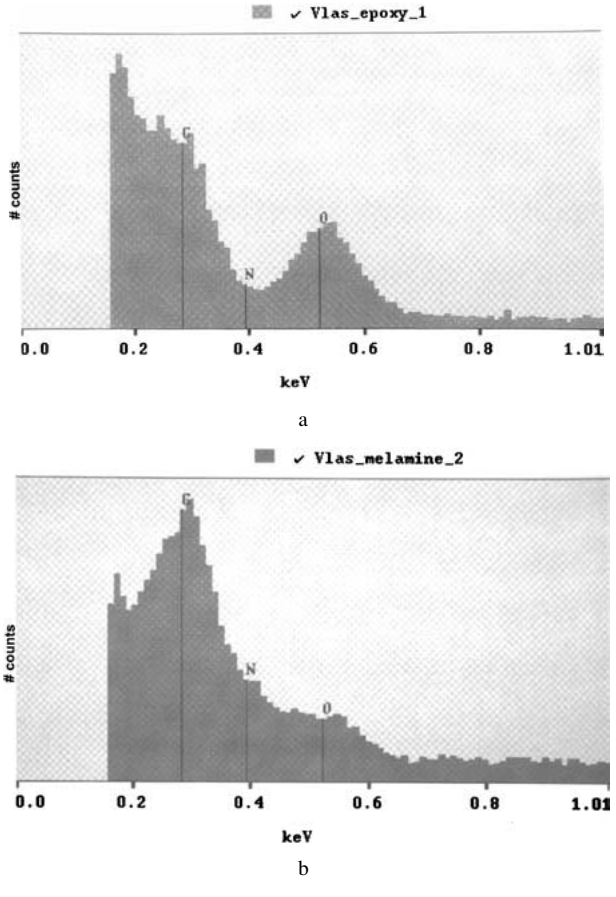


Figure 3 SEM-EDAX plot taken inside a fibre in an epoxy matrix. 4a. Non-treated fibre. 4b. MF-treated fibre.

plots taken inside a fibre in two different flax filled epoxy composites, one with untreated flax fibres (Fig. 3a) and one with MF treated flax fibres (Fig. 3b). Clearly visible is the extra 'knee' of the nitrogen of the MF resin in the sample with MF treated fibres, indicating that indeed the MF resin has actually penetrated into the flax fibre.

The effect that the MF impregnation has on the internal structure of the fibres is shown in Fig. 4. Both Fig. 4a and b show a fibre which is split in length direction. The fibre in Fig. 4a is standard flax and the fibre in Fig. 4b is impregnated with MF. Even though the micrographs have a slightly different scale, it is clearly visible that in non-impregnated flax a lot of damage along the fibrils in the secondary cell wall is present, the fibrils are at some places separated over considerable lengths. In impregnated flax the fibrils seem to have been glued together quite effectively and the fracture surface is rather smooth, even though the underlying fibrillar structure can still be made out. It can therefore be concluded that MF resin indeed fully diffuses into the fibres and is able to form bonds between the fibrils in the secondary cell wall.

Another micrograph is shown in Fig. 5. This fibre is impregnated with MF and subsequently broken in tension. Nicely visible on the fracture surface is the internal structure of the fibre with a size of circa 0.2 μm. An interesting feature is pointed at by the arrow. This lump of material does not have the fine structure that the rest of the fibre has, indicating that it might be the MF resin. Moreover the shape of this lump is similar to the shape of the kink bands as reported by Bos *et al*. [2], a crack bridged by fibrils, with the exception that this is a 'negative' picture of the kink band. It might be that this is actually the MF resin that has filled the holes in a kink band in the fibre, and has cured in this shape.

Based on these results, it can be concluded that the resin inside the fibre is able to stabilise the flax fibres under compressive loading. The fact that MF also appears to be able to stabilise the viscose composite might be caused by the twist present in the viscose yarn. Supposing that MF also penetrates into the viscose, internal cross-linking of the viscose yarn will stabilise the twist and also protect this fibre against too readily deforming in compression.

The treatments also strongly influence the failure mechanisms occurring during the ILSS and compression tests. Generally, it can be stated that with increasing ILSS, and therefore increasing adhesion, the failure mechanism gradually changes from multiple shear to single shear. Samples with a low compressive strength fail little by little whereas the samples with a high compressive strength break instantaneously in the ILSS test as well as in the compression test. This effect is not only brought about by the impregnation with MF but also by the increase in adhesion due to the MA treatment, so it appears to be governed by the increase in adhesion rather than the increase in internal fibre stability due to the MF impregnation step.

Table IV further shows the effect that changing the concentration of MF in the solution in which the fibres are soaked has on the ILSS and the compressive strength of the composites. Increasing the MF concentration in the soaking solution, and therefore increasing the amount of resin on and in the fibres, decreases the ILSS for both the viscose and flax fibre reinforced composites. However, it further increases the compressive strength of the composites. Premature failure of the brittle MF could account for the fact that the ILSS decreases with increasing MF amount. The fact that the compressive strength increases with increasing MF content is now presumably not caused by increased adhesion. Two effects might be present:

1. the MF layer around the fibre is thicker at higher MF contents and thus the resin phase of the composite contains a higher amount of MF resin compared to the amount of epoxy. This will lead to higher compressive strength of the composite (MF resin is known to have a higher compressive strength than epoxy resin),
2. the fibres might contain internally a higher amount of MF resin and have therefore become stronger in compression.

Probably both effects play a role, but it is striking that the fibres are now able to withstand a much higher compressive loading.

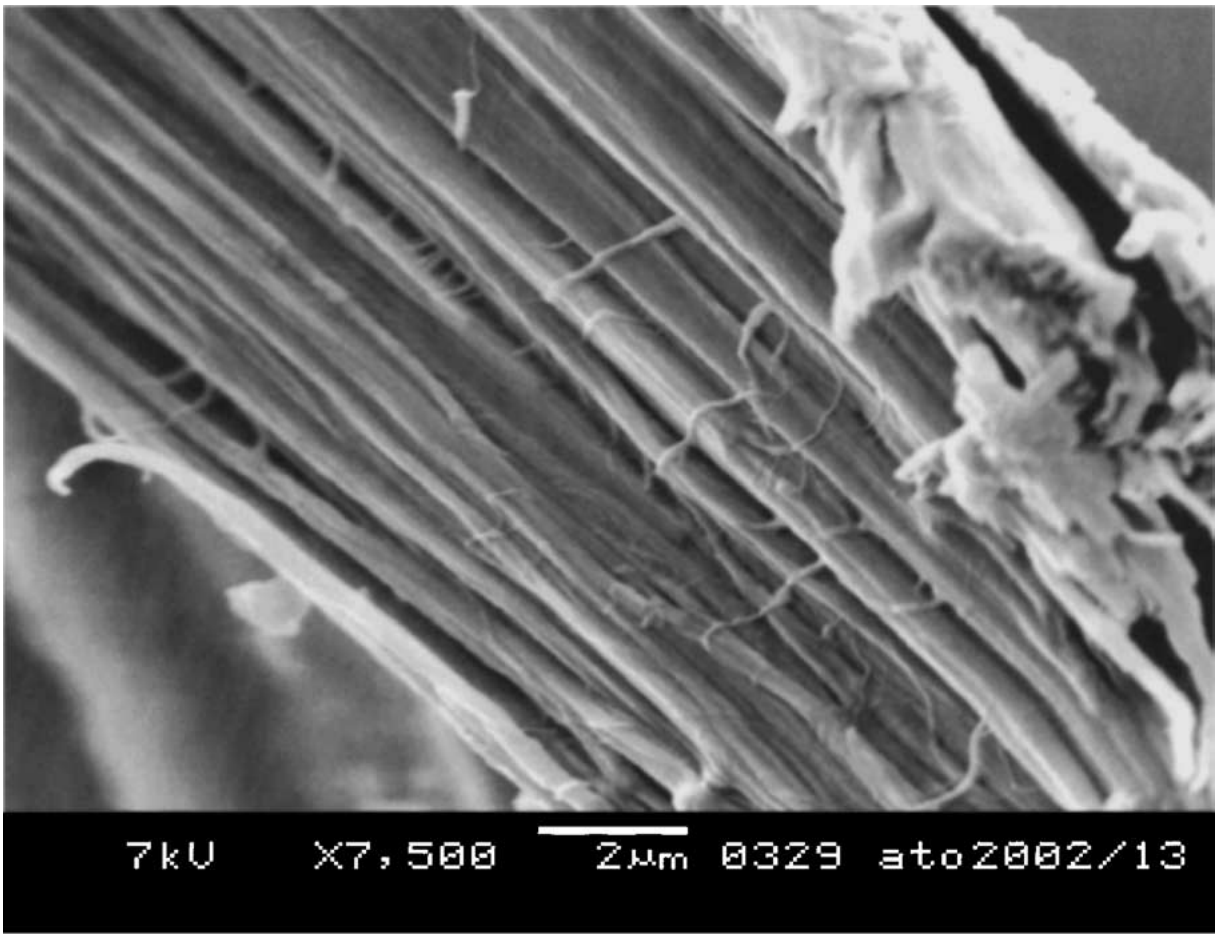
Now it is clear that the compressive strength is increased by the modification of the fibres by MF resin. However, the effect of MF modification on the tensile strength shows a quite different trend. Tensile strength and tensile modulus of both flax and viscose fibres and composites without and with MF treatment are given in Table V. The composites contain in this case 30 wt% fibres. It is clear that, whereas dewaxing has no influence on the strength of flax fibres, the impregnation with MF resin seriously decreases the fibre strength. The same effect is seen in the composite, the tensile strength of the flax reinforced composite with MF resin is lowered dramatically compared to the tensile strength of the unmodified composite. The modulus of the composite seems uninfluenced by the impregnation step. On the other hand, whereas the tensile strength of the viscose fibres is also lowered by the impregnation of the fibres with MF, the strength of the composite is increased by 25% due to the addition of MF.

Possibly, in flax there are regions in the fibre which consist completely of MF resin (in the areas of the kink bands as also indicated in Fig. 5). Under tension the

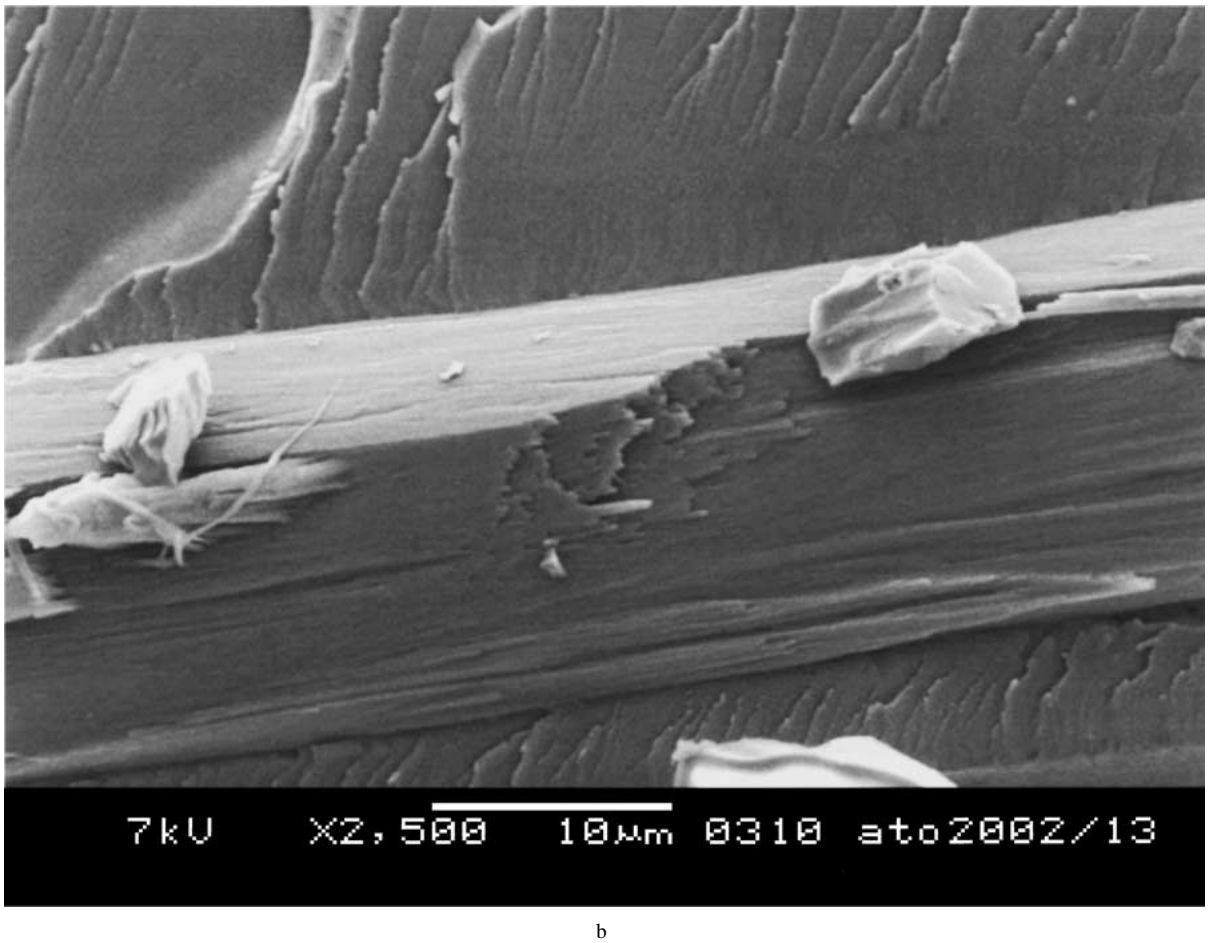
TABLE V Fibre strength and composite tensile strength and modulus without and with MF treatment. Composites contain 30 wt% fibre

Fibre	Fibre strength $\sigma_{tensile}$ (MPa)	Composite strength $\sigma_{tensile}$ (MPa)	Composite modulus $E_{tensile}$ (GPa)
Flax	750 (131)	249 (25)	23.3 (3.3)
Flax dewaxed	820 (52)	242 (28)	18.5 (1.0)
Flax dewaxed + MF[a]	441 (44)[b]	147 (8)	23.9 (0.8)
Viscose	510 (19)	203 (5)	8.9 (0.06)
Viscose dewaxed + MF[a]	336 (34)[c]	256 (7)	11.0 (0.4)

[a]Concentration MF in solution 20%.
[b]This sample contains 26% MF.
[c]This sample contains 42% MF.



a



b

Figure 4 SEM micrographs of flax fibres split in length direction. 5a. Flax fibre (not treated) scale bar represents 2 μm, 5b. Flax fibre impregnated with MF, scale bar represents 10 μm.

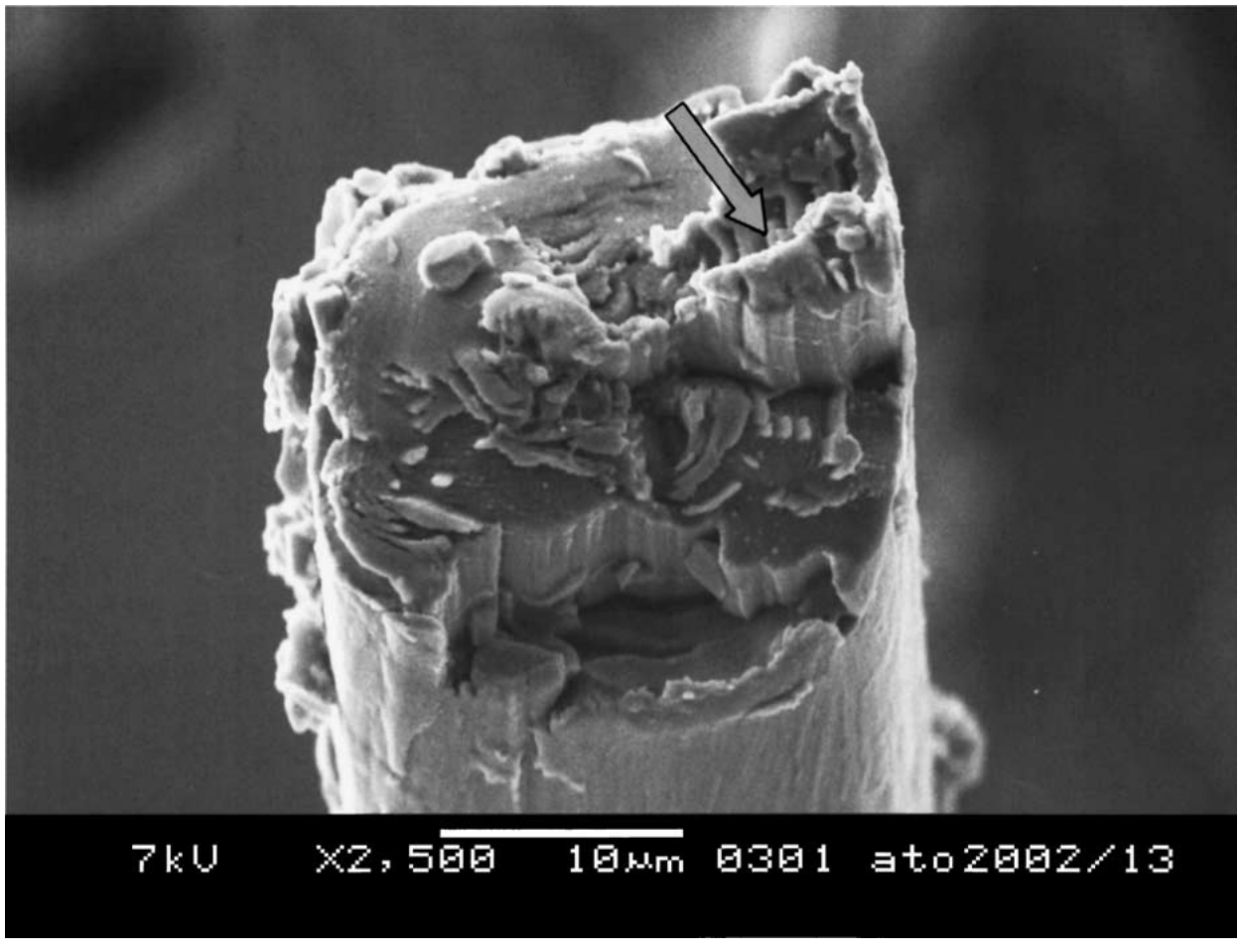


Figure 5 SEM micrograph of a fracture surface of an impregnated fibre. The arrow points at a part of the surface where the fibre structure is not visible and which could be MF resin penetrated into a kink band, scale bar represents 10 μm.

excess of brittle resin in the fibres could lead to early crack formation reducing the strength of the fibre. It is not easy to understand why the viscose composite shows a higher strength with the MF treated fibres, in spite of the reduced strength of the fibre bundles. It can be expected that in the viscose fibres the MF resin is distributed more evenly through the fibres, so that internal stress concentrations in the fibres are less likely to occur than in the flax fibres, the fibres might internally be stronger than the measurements indicate. The strength of the individual fibre bundles could be reduced by surface flaws in the MF layer surrounding the fibre due to the impregnation step. In the composite, the presence of the epoxy resin, fully surrounding the impregnated bundles, could diminish this effect, leading to the increase in tensile strength.

It is interesting to compare these results with experiments performed by Hepworth *et al*. [32], who were able to let epoxy resin penetrate into the flax cell wall after a urea treatment. They find that UD-composites made with these fibres have a 30% higher stiffness but similar strength compared to UD-composites from untreated fibres. They do not report any data on the compressive properties of their materials. The fact that epoxy resin is by itself far stronger than MF resin could account for the fact that in this case the tensile strength does not decrease. The increase in modulus is less easily explained. It is furthermore of interest to note that epoxy is not by itself able to penetrate into the flax cell wall [32].

It can now be expected that the better the MF resin is diffused into the fibres, the higher the compressive strength of the composite will become. Fig. 6 shows compressive strength data of composites containing fibres which were impregnated via different routes, against the total amount of MF present in the composite. Both the time and the temperature of the impregnation step were varied and also two batches of fibres were allowed to pre-swell in water during three hours in order to make them more accessible to the resin. The differences in MF content were reached by changing the concentration of the MF solution.

The MF amount does not seem to be governed by the method of application. Furthermore there is no drop or jump in the compressive strength with changing MF content or with changing method of application, as might be expected when the fibres are not fully filled with resin by some of the application methods.

It is clear that the method of resin application does not have any influence on the compressive strength of the composites, the only governing factor seems to be the total amount of MF resin present in the composite.

It might be that since the fibres are rather thin, the penetration of resin into the fibres is fast enough that 5 min in a 20°C solution is sufficient to ensure effective impregnation of the fibres. The fact that kink bands

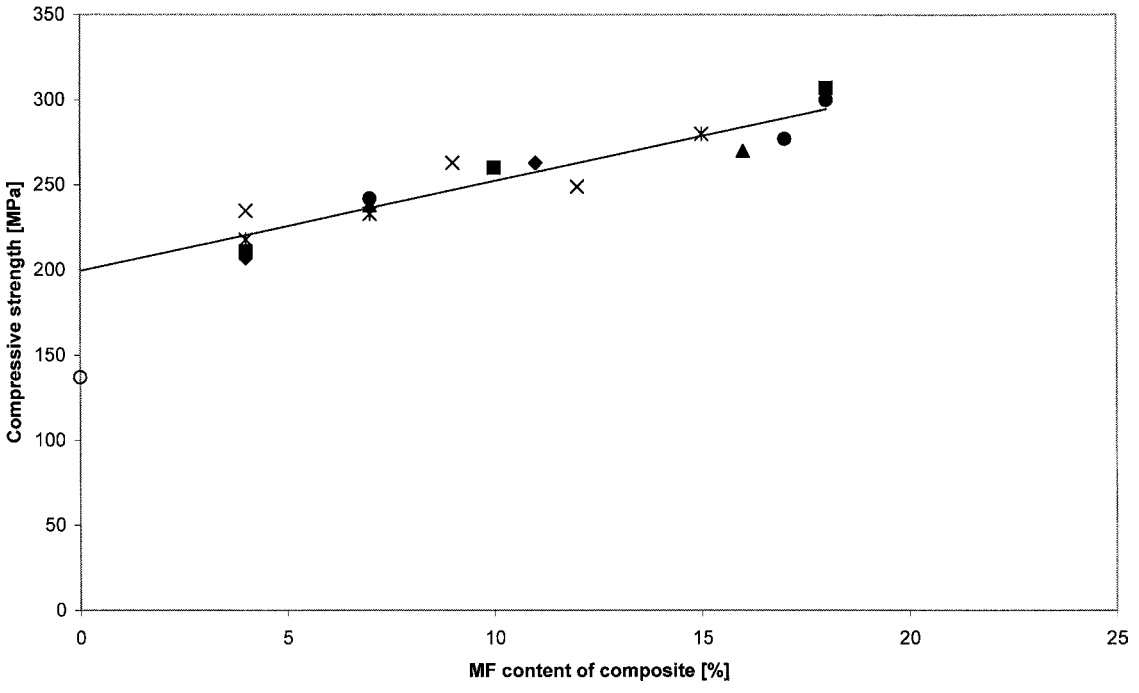


Figure 6 Compressive strength vs. MF content in the composite. Influence of the impregnation method. ♦ 20°C, no pre-swell, 5 min in MF. ■ 20°C, 3 h pre-swell in water, 5 min in MF. ▲ 20°C, no pre-swell, 1 h in MF × 70°C, no pre-swell, 5 min in MF. × 70°C, 3 h pre-swell in water, 5 min in MF. ● 70°C, no pre-swell, 1 h in MF. ○ no MF treatment. The solid line gives the trend taking all data but the blank.

often end just under the very thin primary cell wall which forms the fibre surface [5], might indeed make the fibres and especially the kink bands very easily accessible for the resin.

If it assumed that all fibres in Fig. 6 are equally impregnated the values can be compared. The solid line gives the mean trend of the compressive strength with the amount of MF in the composite. As mentioned before, MF resin is expected to have a higher compressive strength than epoxy resin (roughly ca. 275 MPa vs. ca. 82 MPa). The rise in compressive strength is found to be ca. 5.3 MPa per percent MF resin, this is more than expected based on the rule of mixtures, again indicating that the addition of MF resin has an additional effect on the compressive strength of the fibres. Moreover, there is a sharp rise in the compressive strength going from 137 MPa for the composite with dewaxed fibres, without MF to over 200 MPa for the composites with MF. This again supports our view that the MF resin actually is able to fill the hole-like defects that are present in the fibres due to the decortication process and also cross-link the fibres internally and thus stabilise the fibres under compression. A very rough estimation for the compressive strength of the fibres can be derived using the estimated values for compressive strength for MF resin of 275 MPa and for epoxy resin of 82 MPa, the rule of mixtures (not taking into account the differences in density of the three materials) then gives a value for the compressive strength of the stabilised fibres of ca. 400 MPa. This is still much lower than the compressive strength of 1200 MPa as measured on single elementary flax fibres by Bos *et al*. [2] in a loop test.

4. Conclusions

The wax layer that is normally present around flax fibres prohibits the reaction of the fibres with a resin like epoxy or a reactive molecule like MA. Only after the wax layer is removed it is possible to form a proper bond between fibres and matrix.

Compressive strength of unidirectional composites of flax is low due to the presence of kink bands in the fibres, which are formed during the isolation steps, by which the fibres are separated from the plant. Merely improving the adhesion between flax fibres and the matrix is not sufficient to improve the compressive strength.

It is possible to stabilise the fibres in compression by impregnating them with an MF resin. The resin diffuses into the fibre, filling the holes that are present in the kink bands and also cross-linking the fibre internally and thus stabilising the fibres under compressive loading. Unfortunately the impregnation with MF resin seriously reduces the tensile strength of the fibres and the resulting composite, making this route as yet unsuitable for the production of structural composites from flax fibres.

Impregnation of the fibres with the resin is completed within a few minutes, probably due to the small dimensions and relatively open structure of the flax fibres.

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