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The manufacture and mechanical testing of thermosetting natural fibre composites

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High volume fraction hemp and flax fibre composites were manufactured using low viscosity epoxy and phenolic resins. Using 80% volume fraction of flax fibres in epoxy resin, composites with a mean stiffness of 26 GPa and a mean strength of 378 MPa were produced. By reducing processing damage of the plant fibres mechanical properties could be increased by 40%. Strips of retted fibre tissue were found to be just as effective for reinforcement as fibre bundles and individual fibres. Phenolic resin and decorticated flax fibres produced very poor composites. Using 40% volume fraction of fibres the mean stiffness was 3.7 GPa and the mean strength was 27 MPa. Two fibre pre-treatments were devised to improve adhesion with resins. The first, 6 M urea was used only in natural fibre-epoxy composites where it increased the stiffness but not the strength. The second pre-treatment was a 50% PVA solution, which was cured prior to the addition of space filling resin. The PVA treatment improved the stiffness and strength of both natural fibre-epoxy composites and natural fibre-phenolic composites.

1. Introduction

Natural fibres from plants like hemp and flax have the potential to be used as glass fibre replacements in certain composite applications. The mechanical properties of many plant fibres and plant fibre composites have been described [1–11]. Much of the early work used thermosetting resins for the matrix material, but in the last 10 years a lot of work has been done using polypropylene and polyethylene thermoplastics. Many of these investigations have been aimed at applications where the quality of fibre is less important than keeping the manufacturing costs to a minimum (the margins are smaller). In many cases low volume fractions of short fibres provide sufficient reinforcement and can be achieved relatively easily and cheaply [5, 12]. However to get a good reinforcing effect using these plastics it is often necessary to increase the adhesion between the fibres and resin by using fibre surface treatments [4, 10, 13].

Epoxy and phenolic thermosetting resins are known to be able to form covalent crosslinks with plant cell walls via hydroxyl groups, unlike polypropylene or polyethylene [14]. Composite manufacture can be achieved using low viscosity epoxy and phenolic resins that cure at room temperature. Therefore although these resins are relatively expensive they have potential for the development of high added value plant fibre composites, where long fibres at a high content are required. Products like Tufnol which is made from cotton fibres and epoxy resin, have been available for some time and have good stiffness and strength [15]. In the last few years there has been renewed interest in these products for use in the automotive industry [8]. However the influence of fibre quality, fibre volume fraction and methods of production in high added value, high fibre content natural fibre composites have been less well characterised. For example how does the damage to fibres, which occurs during the extraction processes [16] affect stress distributions within fibres once they have been embedded in resin? Does it matter whether the fibres are single or exist as bundles? The economic significance of the processing and treatments are often not taken into account. Natural fibre is potentially more cost effective than glass and has an environmentally friendly image. However this advantage is lost if the fibres are subjected to expensive chemical and physical treatments before being embedded. Processing damage reduces their value, while surface treatments and methods of turning the fibres into mats and cloths all increase the cost.

In this paper low cost methods were used to try to improve the properties of high value, high fibre content natural fibre composites. Damage to fibres, degree of retting, fibre surface treatments, fibre volume fraction and methods of manufacture were all considered.

2. Methods

Hemp and flax stems and fibre were obtained from the Silsoe Research Institute. Fibre was obtained from retted tissue using a mechanical decorticator [17] and was composed mostly of bundles of fibres (cells). This

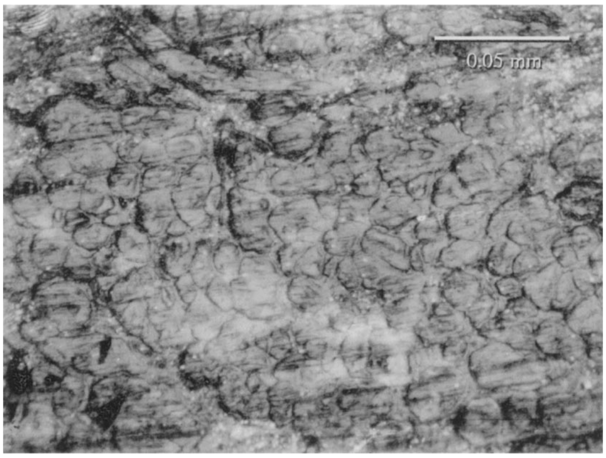


Figure 1 Photograph of a transverse section through a flax-epoxy composite (retted mechanically decorticated flax).

was compared with strips of fibre which were carefully extracted by hand from retted or unretted stems. Retting was carried out in a controlled environment; a vat of continuously stirred liquor (water that had been used previously for retting) at 20 °C.

A low viscosity epoxy system, which incorporates a slow hardener, was used to make composites (S.P. Systems Ampreg 26). The resin and hardener were thoroughly mixed in a ratio of 3 parts resin to 1 part hardener and then de-gassed in a reduced pressure environment (not a full vacuum because this accelerates the curing reaction). The fibre was orientated by hand combing repeatedly in a single direction. The fibre was then placed into a simple mould (Fig. 1) which had been coated with PTFE release agent and the epoxy resin was poured over the fibre. The epoxy was left for 10 min to soak into the fibre mat. Trapped air was gently squeezed out of the mat using a wide flat-ended metal probe to reduce possible damage. The fibre and resin was then left for 30 min to allow the air bubbles which had been squeezed out of the fibre mat to escape from the surface of the resin. Finally a steel top was placed on the mould. The volume fraction of fibre in the composite could be controlled by adding known weights of fibre and resin and by applying different amounts of pressure to the mould using G-clamps. The composite was left to cure for 48 h before being removed from the mould. Post curing was continued for a further 4 h in an oven at 60 °C.

Some fibre was soaked in 6 M Urea for 24 h. The water in the fibre cells was replaced by taking them through a graded series of increasing concentrations of alcohol. 95% alcohol could also be mixed with the resin (1 part to 4 parts resin) to reduce the viscosity and allow miscibility with alcohol in the cell walls (refer to paper I). Mixing alcohol with resin increased the curing time at 20 °C by several days.

Liquid phenolic resin was also used (Blagden Chemicals, J2027L with phencat 382 catalyst in a ratio of 20 : 1 by weight). The same moulds and preparation procedure as those used for the epoxy resin were applied, except that a wax release agent was used. An alternative method was also developed which did not require pressures to produce high volume fraction composites. Bunches of combed decorticated flax fibres were pretreated with a 50% mix of PVA (Unibond) and water. The PVA mix was absorbed by the fibres which were then hand pressed into a thin mat. This mat was dried out at 100 °C for 1 h until all the water had been driven off and the PVA was hard. Epoxy or phenolic resin was then run over the mat and the excess squeezed out by hand rollering. The mat was cured as previously described.

The cured composites were cut into dumbbell shaped specimens, which were fitted with strain gauges and stretched in an Instron 4202 testing machine. Parameters such as strength, failure strain and Young's modulus were recorded.

Transverse sections of untested composites were cut using a fine toothed band saw and then finely polished using 40 μm grit sandpaper. The sections were mounted under a light microscope with a camera, which was connected to a PC. The interface between the fibres and the resin was examined visually and the volume fraction of fibre was accurately measured using an image analysis package.

The density of the composites was measured using displacement of a liquid when a known weight of composite was immersed. Epoxy resin was used as the liquid because this does not penetrate the fibres.

3. Results

Untreated, retted, mechanically decorticated fibre from both hemp and flax plants, embedded in epoxy resin at a volume fraction of 0.5, produced composites with strengths and moduli 3–4 times greater than cured resin which has a strength of 60 MPa and a tensile modulus of 3 GPa (Table I). Transverse sections of composites examined with a light microscope showed that there was good contact between the fibres and the resin (Fig. 1). However the resin did not penetrate into cell lumens or into fibre bundles. Curing the resin with fast hardener resulted in a flax composite with greatly reduced modulus (Table I).

Urea treatment increased the modulus of the flax composites by 30% (Table I), while urea treatment followed by replacing the cell wall water with alcohol increased the modulus by 40%. The strength was unaffected by these treatments. Photographs of transverse sections showed that the adhesion between the fibres and the resin was very good after urea and alcohol treatment (Fig. 2). The resin was seen to have penetrated into fibre bundles.

Composite moduli and strengths are plotted as a function of fibre volume fraction (V_f) for flax-epoxy composites in Fig. 3. Increasing the volume fraction of fibre increases the strength and modulus and in both cases the curves show an increasing slope at volume fractions greater than 0.4.

Using strips of fibre tissue to make composites produced the following results. With unretted strips of flax and hemp tissue the modulus of the composite was low. In many places there was no adhesion between the fibre strips and the resin (Fig. 4a). The resin did not penetrate into the fibre strips. Adhesion was poorest on the outside

TABLE I The mechanical properties of natural fibre composites with a fibre volume fraction of 50%. M = mean, S = standard deviation, n = number of samples tested

Treatment	E composite (GPa)	V_f	Strength (MPa)	Fibre orientation (°)
Retted, mechanically decorticated flax, 3 : 1 (slow)	$M = 11.86$ $S = 1.69$ $n = 5$	$M = 0.49$ $S = 0.01$ $n = 5$	$M = 118.5$ $S = 6.03$ $n = 5$	$M = 14.86$ $S = 6.49$ $n = 5$
Retted, mechanically decorticated flax, 3 : 1 (fast)	$M = 6.74$ $S = 0.04$ $n = 3$	$M = 0.50$ $S = 0$ $n = 4$	$M = 58.7$ $S = 1.53$ $n = 4$	
Retted, mechanically decorticated hemp, 3 : 1 (slow)	$M = 9.6$ $S = 1.0$ $n = 4$	$M = 0.5$ $S = 0.02$ $n = 4$	$M = 145$ $S = 8.6$ $n = 4$	
Retted, mechanically decorticated flax, urea, 3 : 1 (slow)	$M = 13.96$ $S = 0.1$ $n = 4$	$M = 0.49$ $S = 0.01$ $n = 4$	$M = 121.5$ $S = 1.9$ $n = 4$	$M = 7.9$ $S = 0.9$ $n = 4$
Retted, mechanically decorticated flax, urea, 95% alcohol, 3 : 1 : 1 (slow)	$M = 14.82$ $S = 0.55$ $n = 4$	$M = 0.48$ $S = 0.01$ $n = 4$	$M = 118$ $S = 5.6$ $n = 4$	$M = 11.6$ $S = 4.8$ $n = 4$

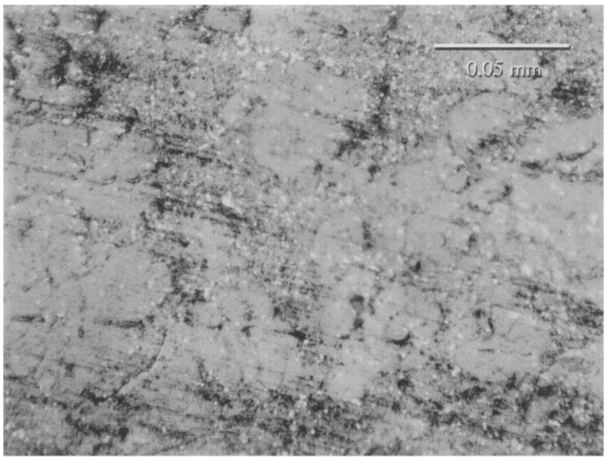


Figure 2 Photograph of a transverse section through a flax-epoxy composite in which the fibre had been pre treated with urea and alcohol.

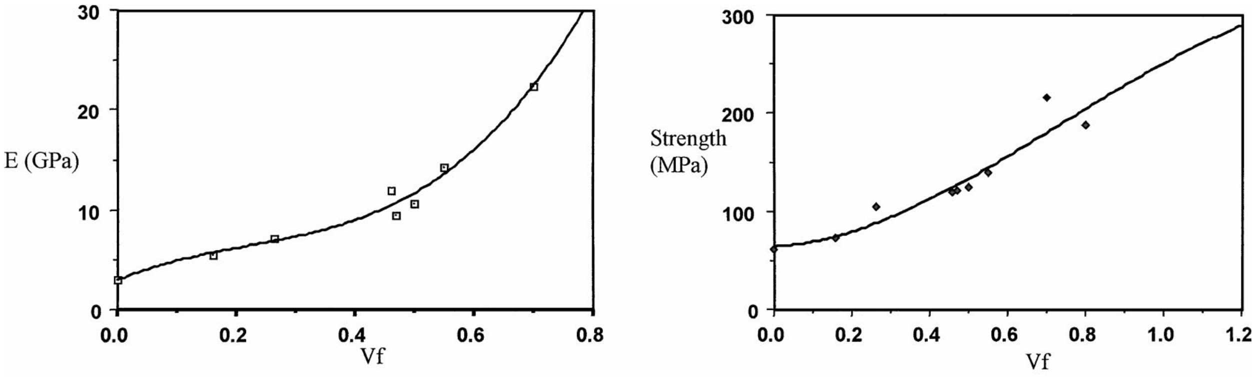
TABLE II The mechanical properties of composites made from strips of fibre tissue. M = mean, S = standard deviation, n = number of specimens tested

Treatment	E composite (GPa)	V_f	Strength (MPa)	Fibre orientation (°)
Unretted, strips hemp tissue, 3 : 1 (slow)	$M = 4.5$ $S = 0.3$ $n = 3$	$M = 0.50$ $S = 0.023$ $n = 3$	$M = 62$ $S = 1.15$ $n = 3$	0
7 days retting. Strips hemp tissue. 3 : 1 (slow)	$M = 12.65$ $S = 2.27$ $n = 4$	$M = 0.5$ $S = 0.01$ $n = 4$	$M = 145.5$ $S = 8.1$ $n = 4$	0
Unretted, strips of flax fibre tissue, 3 : 1 (slow)	$M = 4.65$ $n = 2$	$M = 0.5$ $n = 2$	$M = 59.5$ $n = 2$	$M = 2.1$

of the strips where there is a waxy cuticle. However after 7 days retting of hemp stems the fibre tissue was used to make composites with a much higher modulus (Table II). This is because the resin begins to penetrate into the fibre tissue between the bundles where microbial degradation has caused gaps to appear (Fig. 4b). The composites made from strips of retted hemp tissue had a higher modulus than those made from decorticated fibre.

Using high volume fractions of fibre (0.7 or more), composites with moduli greater than 20 GPa and strengths greater than 200 MPa were produced (Table III). The best composite, with a modulus of 26 GPa and a strength of 378 MPa, was produced by treating strips of retted flax tissue with 6 M urea, replacing the water with alcohol and then embedding in a mixture of resin and alcohol (Table III). These composites had a lower modulus and strength than chopped strand glass fibre made in a similar way and with similar volume fractions of fibre (Table III). However taking the density of the composites into account (Tables IV and V), in terms of specific modulus, the natural fibre composites are comparable to glass fibre composites. Where they are not as good is with regard to the specific strength.

Fig. 5 shows the density of flax composite as a function of fibre volume fraction. The density decreases



(a) (b)

Figure 3 Graphs showing the modulus and strength of flax-epoxy composites as a function of the volume fraction of fibre. (a) Modulus. (b) Strength.

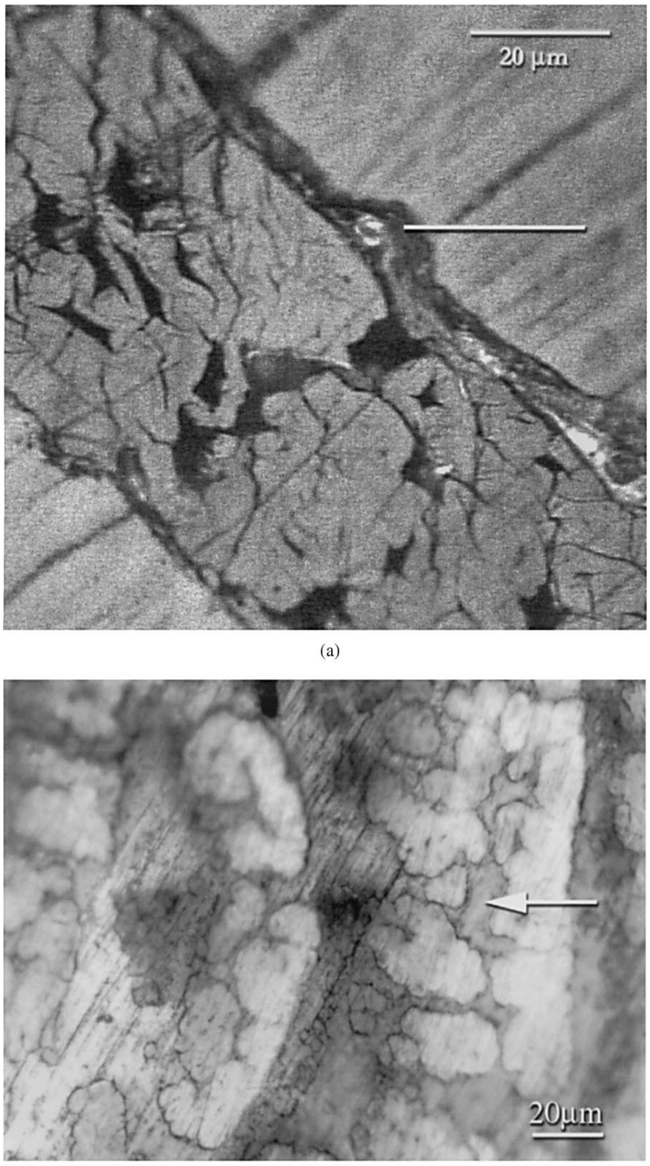


Figure 4 Photographs of a transverse section through a flax-epoxy composite made from strips of fibre tissue. (a) Unretted flax tissue used. (b) Retted flax tissue used. The arrows indicate where resin has penetrated into the fibre strips and the lines show where the resin has shrunk away from the cuticle.

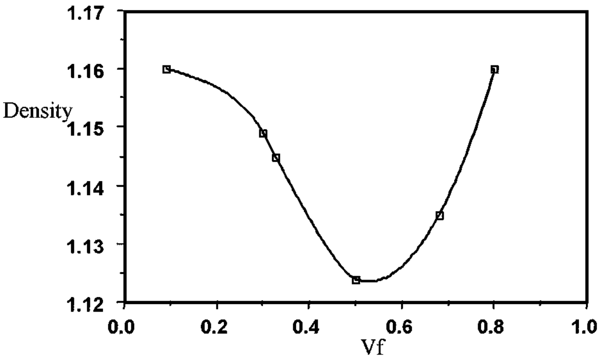


Figure 5 The density of flax-epoxy composite as a function of the volume fraction of fibre.

with increasing fibre content up to a volume fraction of 50%. However beyond 50% fibre content the density increases.

In order to reduce processing an attempt was made to make a pre formed mat of fibre which would not swell when epoxy resin was added. PVA, diluted by 50% in water was found to be an effective pre-treatment (see method). It reduced the processing complexity by allowing pre formed mats of fibres held together with cured PVA to be made. These mats could not swell when epoxy resin was added and therefore fibre volume fractions of 0.4 could easily be achieved. The resulting composites had a better modulus and strength than any other composites at that volume fraction (Table VI). The resin was able to penetrate into the structure of the pre formed mats and make a good bond with the PVA.

Flax fibre embedded in phenolic resin did not produce a composite with properties significantly better than cured resin on its own (Table VII). However pretreatment with PVA improves the composite properties, allowing the volume fraction of fibre to be increased and doubling the stiffness and strength (Table VII).

4. Discussion

Without any pre-treatments flax fibres can be combined with epoxy resin to make composites with high modulus

TABLE III The mechanical properties of individual composites made with high (greater than 50%) volume fractions of fibre

Composite	E (GPa)	Failure stress (MPa)	Failure strain	V_{f}
Retted, mechanically decorticated hemp, 3 : 1 (slow)	21.65	188	0.0195	0.85
Retted, mechanically decorticated hemp, 3 : 1 (slow)	18.27	190	0.0224	0.85
Retted, mechanically decorticated flax, 3 : 1 (slow)	22.45	216	0.0156	0.68
Retted, mechanically decorticated flax, 3 : 1 (slow)	21.3	187	0.0164	0.8
Retted, hand extracted strips of flax. Urea, 95% alcohol, 3 : 1 (slow)	25.97	378.3	0.0163	0.8
Glass, 3 : 1 (slow)	27	379	0.0203	0.5
Glass, 3 : 1 (slow)	34	527	0.0193	0.6
Glass, 3 : 1 (slow)	32.85	512.6	0.016	0.6
Glass, 3 : 1 (slow)	41.0	676.2	0.0175	0.65

TABLE IV The density of flax and glass fibre composites

Composite	Density	V_{f}
Retted, mechanically decorticated flax, 3 : 1 (slow)	1.16	0.09
Retted, mechanically decorticated flax, 3 : 1 (slow)	1.149	0.3
Retted, mechanically decorticated flax, 3 : 1 (slow)	1.145	0.326
Retted, mechanically decorticated flax, 3 : 1 (slow)	1.124	0.5
Retted, mechanically decorticated flax, 3 : 1 (slow)	1.135	0.68
Retted, mechanically decorticated flax, 3 : 1 (slow)	1.16	0.8
Retted hand extracted strips of flax tissue, urea, 95% alcohol, 3 : 1 : 1 (slow)	1.187	0.8
Retted, mechanically decorticated hemp, 3 : 1 (slow)	1.12	0.85
Glass, 3 : 1 (slow)	1.7	0.5
Glass, 3 : 1 (slow)	1.88	0.6
Glass, 3 : 1 (slow)	1.86	0.6
Glass, 3 : 1 (slow)	1.9	0.65

TABLE V Density corrected modulus, strength and energy absorption of flax and glass fibre composites

Composite	E/density	Failure σ/density
Retted, mechanically decorticated hemp, 1 : 3 (slow)	19.33	168
Retted, mechanically decorticated hemp, 1 : 3 (slow)	16.31	170
Retted, mechanically decorticated flax, 1 : 3 (slow)	16.69	134
Retted, mechanically decorticated flax, 1 : 3 (slow)	19.78	190
Retted strips of flax, urea, 95% alcohol, 1 : 3 : 1 (slow)	18.36	161
Retted, mechanically decorticated flax, 1 : 3 (slow)	18.81	274
Glass, 1 : 3 (slow)	16.0	223
Glass, 1 : 3 (slow)	18.1	280
Glass, 1 : 3 (slow)	17.66	276
Glass, 1 : 3 (slow)	22.4	356

TABLE VI The mechanical properties of flax composite made using PVA pre treatment and epoxy resin

Type of sample	E (GPa)	Strength (MPa)	Failure strain	V_{f}
Retted, mechanically decorticated flax, PVA, epoxy	$M = 10.16$ $S = 0.7$ $n = 4$	$M = 156$ $S = 6.6$ $n = 4$	$M = 0.019$ $S = 0.001$ $n = 4$	$M = 0.4$ $S = 0.02$ $n = 4$

TABLE VII The mechanical properties of flax composites made using phenolic resin

Type of sample	E (GPa)	Strength (MPa)	Failure strain	V_{f}
Retted, mechanically decorticated flax, phenolic	$M = 3.8$ $S = 0.7$ $n = 3$	$M = 27.4$ $S = 1.8$ $n = 3$	$M = 0.008$ $S = 0.0013$ $n = 3$	$M = 0.32$ $S = 0.029$ $n = 3$
Retted, mechanically decorticated flax, PVA, phenolic	$M = 6.5$ $S = 1.15$ $n = 4$	$M = 62.3$ $S = 4.46$ $n = 4$	$M = 0.011$ $S = 0.003$ $n = 4$	$M = 0.39$ $S = 0.02$ $n = 4$

and strength, provided that a slow curing agent is used. Rapid curing may not allow the resin to penetrate between fibres as effectively and may also generate higher internal stresses. It is not surprising that good composites can easily be made using epoxy resin because estimates that we made using fibre pull out tests (not reported here) indicated that the critical transfer length of flax fibres (cells) in epoxy resin is less than 1 cm, while their actual length is 2–5 cm. The length of pieces of fibre tissue is variable in the mechanically decorticated material, but most pieces are more than 10 cm long and contain many fibres, which are well bonded together. The interfacial strength within these bundles of fibres is probably greater than the interfacial strength between the resin and the fibres. Therefore it does not matter much that the fibre in the decorticated samples is not composed of separate individual cells. This theory was tested further by using strips of fibre tissue to make composites. Composites, which were just as good or in some cases better than composites made from decorticated fibre were produced but only with, retted strips of fibre tissue. When using unretted tissue the epoxy resin did not adhere to the outer cuticle of the fibre strips. The result was that there were weak interfaces or even gaps between the fibre and resin which reduced the modulus and strength of the composites. When strips of retted tissue were used the cuticle on the outside of the stem had been degraded and in many cases detached from the underlying tissue. The structure of the tissue also became more open due to the removal of material by microbial activity. This allowed the resin to penetrate into the fibre strips after retting resulting in a more effective reinforcement (Fig. 4). Presumably the interfaces which escaped total microbial breakdown were still of sufficient strength for effective stress transfer.

The damaged regions in the mechanically decorticated fibre reduce the stress carried by the fibre bundles [16] and therefore reduce the strength and modulus of the composite. This is why undamaged strips of retted fibre tissue, which have not been through the decortication process can in some instances, provide better reinforcement. Using fibre with little damage at a high volume fraction it should be possible to produce composites with a modulus of 30 GPa and a strength of 500 MPa.

When stiffness and strength are plotted against fibre volume fraction for flax composites “J shaped” curves are produced. Based on previous work a linear response had been expected [11]. One reason for this could be that at low fibre volume fractions the pressures required for processing are small and as a result the fibres may be less well orientated.

The density of flax fibre composites decreases with increasing fibre content up to a volume fraction of 50%. This is because the fibres are hollow and have a lower density than the epoxy. However beyond 50% volume fraction high pressure is required during the processing to maintain a high fibre content. This pressure causes collapse and densification of the fibre cross sections and hence the density of the composites rises. However it does not appear to reduce the effectiveness of the fibres for reinforcement.

Using epoxy resin and flax fibre, materials, which rival glass fibre composites, can be produced. The adhesion between the natural fibres and the resins is good enough for the fibres to act as effective reinforcing agents. However there are problems in terms of the processing. Because of the low density of the natural fibres they float up in the resin before curing and needled mats tend to swell. This means that in order to obtain fibre volume fractions greater than 20%, pressure needs to be applied during the curing process. What is required is a pre-treatment which can wet the fibres or fibre mat and allow them to be hand pressed and cured to form a higher density sheet. Such a pre treatment can be achieved with 50% PVA in water.

Unexpectedly flax fibres did not significantly reinforce phenolic resin. There could be several reasons for this, for example low interfacial strength. Further investigation will be needed to clarify this. However it was found that PVA treatment enabled a better phenolic-flax composite to be manufactured, with increased fibre volume fraction and increased stiffness and strength. This more than doubled the values of stiffness and strength for the composites. PVA is therefore a good all round pre treatment when making thermosetting flax fibre composites

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