# THE USE OF FUNGAL TREATMENT FOR MODIFICATION OF INDUSTRIAL HEMP FIBRE FOR USE IN COMPOSITES

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## Abstract

Industrial hemp fibre is one of the strongest and stiffest available natural fibres and therefore has great potential in composite materials [1]. Incorporated into a thermoplastic matrix, it gives a structural material that is cheap, light-weight and recyclable. However, natural fibres are commonly incompatible with common moulding thermoplastics such as polypropylene, which limits the performance of the composites produced. The main objective of the current work was to investigate the use of fungi to treat hemp fibre to create better bonding characteristics in natural fibre reinforced polypropylene composites. X-ray diffraction (XRD), lignin testing, thermal analysis and scanning electron microscopy (SEM), were used to characterise the effect of treatment on hemp fibres. A combined alkali and fungal fibre treatment produced a composite tensile strength of 48.3 MPa representing a 32% increase, as well as increased thermal stability, compared to composites with untreated fibre.

## Introduction

Industrial hemp has a number of advantages over other crops, being naturally pest resistant, able to smother weeds when grown at a density suitable for producing high quality structural fibre and once planted, requires no effort until harvest [2]. At the top end of the natural fibre performance spectrum, it competes well with glass fibres on a specific strength and stiffness basis, which lends it to being a sustainable alternative in many applications [3]. However, a major challenge for hemp fibre is obtaining good interfacial bonding with common moulding thermoplastics including polypropylene. The most successful approach has been to use maleated polypropylene as an addition to polypropylene which increases its hydrophyllicity, thus making it more compatible and also enabling covalent and hydroxyl bonding with natural fibre [4]. In addition, to improve interfacial bonding, modifications can be made to the fibres. Most work in this field has used chemical methods to remove lignin and other non-cellulosic material to increase access of cellulose hydroxyl groups which can take part in bonding as well as for chemical coupling itself [5]. Although hemp fibre surface chemical treatment has been somewhat successful in improving interfacial bonding, the properties are not fully reflected in the composite properties. There are also unresolved pollution problems with chemical disposal after treatment, plus chemical treatment cost. However, relatively unexplored, fungi could provide a low cost, efficient and environmentally friendly alternative to bring about desirable modification in terms of improved chemistry and morphology. A number of studies have been carried out on the application of fungi in the paper industry for pulping and bleaching of different wood and non–wood raw materials such as straw 7.

It is estimated, that on a worldwide basis, there are about 1.5 million species of fungi, commonly classified into four groups, namely, Basidiomycetes, Ascomycetes, Zygomcetes and Deuteromycotes. White rot fungi, from the Basidomycetes group, have been the only fungi

shown to degrade lignin to expose the cellulose and hemicellulose for metabolising [6]. They do this by producing extracellular oxidases that degrade not only lignin, but also an extensive range of other non-lignin related aromatic and non-aromatic compounds. The most important lignin degrading enzymes are lignin peroxidases (LiP), manganese peroxidases (MnP) and laccases [7]. It has also been reported that some white rot fungi can also remove pitch components from fibre [8]. Fungi belonging to the Ascomycetes group, are known to degrade the pitch component of natural fibres by producing lipolytic enzymes (lipase) which has also been shown to increase fibre strength [9,10]. Fungi belonging to the Zygomycetes group are not thought to break down lignin, but break down pentachlorophenol (PCP) [11], which has a similar structure to lignin, so the pathways for degradation might be expected to be similar. The main objective of the project was to investigate fungal treatment methods which could be applied to hemp fibre in order to create better bonding fibre for natural composite materials.

# Experimental

## Materials

Industrial hemp (Cannabis sativa L.) from a single crop grown in the Hawkes bay region of New Zealand was used in this investigation. It was harvested after seed production and allowed to partially ret in the field. Five different fungi were utilised in fibre treatment, detailed in Table 1. Analytical grade sodium hydroxide pellets (98% purity) were used in the alkali treatment of the fibres. Polypropylene (Icorene® PP CO14RM) with a density of 0.9g/cm$^3$, supplied by Aldrich Chemical was used as the composite matrix; and A-C 950P, a high molecular weight MAPP, supplied by Honeywell International Inc, USA, was used as the coupling agent.

*Table I: Summary of Fungi Used for Fibre Treatment*

| Name | Group | Abbreviation |
|---|---|---|
| *Phanerochaete sordida* | *Basidomycetes* (white rot fungi) | D2B |
| *Pycnoporus species* | *Basidomycetes* (white rot fungi) | Pyc |
| *Schizophyllum commune* | *Basidomycetes* (white rot fungi) | S.com |
| *Absidia* | *Zygomycetes* | B101 |
| *Ophiostomn floccosum* | *Ascomycetes* | F13 |

## Fibre Treatment

Alkali fibre treatment was carried out in a 10% NaOH solution with a maximum processing temperature of 160$^o$C as described elsewhere [12]. Then fibres were washed and dried in an oven at 80$^o$C for 48 hours. For fungal treatment, hemp fibre was initially sterilised in an autoclave for 15 minutes at 120$^o$C. The fungi:hemp ratio was approximately 10 mg fungi:12 g sterilised hemp and incubation was carried out at 27$^o$C for 2 weeks. After treatment, the fibres were sterilized and washed in a fibre washer for 10 minutes before being dried in an oven at 80$^o$C for 24 hours prior to tensile testing and characterization.

### Lignin Testing

The amounts of acid-insoluble lignin and acid-soluble lignin were measured using TAPPI Standard Methods T 222 om-88 and TAPPI Useful Method UM 205 respectively.

### X-Ray Diffraction

Fibre was cut finely to produce a powder, pressed into disk and analysed using a Phillips X'Pert-MPD system over a range of 2θ values from 10 to 50$^{o}$ at a scanning speed of 0.03 mm/s.

### Thermal Analysis

Untreated and treated fibre samples weighing between 6 and 13 mg were analysed using an Instruments SDT 2910 thermal analyzer operated in a dynamic mode, heating from ambient temperature to 500$^{o}$C at 10$^{o}$C /min in air purged at 150 ml/min with an empty pan used as a reference. Differential thermal analysis (DTA) curves and thermal gravimetric analysis (TGA) curves were obtained.

### Single Fibre Tensile Testing

Single fibres were tensile tested in accordance with ASTM D 3379-75 Standard Test Method for Tensile Strength and Young's Modulus for High-Modulus Single Filament Materials at a rate of 0.5mm/min, testing 20 samples at each treatment level. Fibre diameters were measured (average of six readings equally spaced along fibre) using an optical microscope at 200X magnification.

### Composite Fabrication

Fibre was guillotined into 10mm lengths. Fibre, polypropylene and maleated polypropylene (MAPP) coupling agent were dried at 70$^{o}$C for 48 hours, then compounded at 3wt% MAPP and 40wt% fibre content using a ThermoPrism TSE-16-TC twin-screw extruder, pelletised, dried at 70$^{o}$C for a further 48 hours and then injection moulded using a BOY 15-S injection moulder into composite tensile test specimens. Tensile test specimens were conditioned at 20$^{o}$C and 50% relative humidity for 48 hours prior to tensile testing using an Instron-4204 tensile testing machine with a 5kN load cell, operated at a rate of 5mm/minute using an Instron 2630-112 extensometer to measure the strain with 12 specimens of each composite type.

## Results & Discussion

### Fibre Morphology

The untreated fibre surface appeared generally smooth and glossy, due to being coated with non-cellulosic material, mainly lignin, but also waxes, oils and other traces of material standard for cellulosic fibres (see Figure 1).

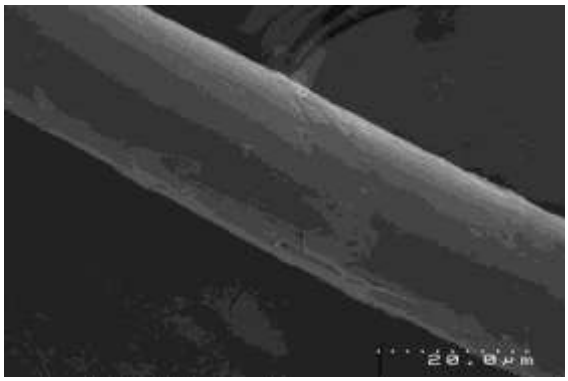
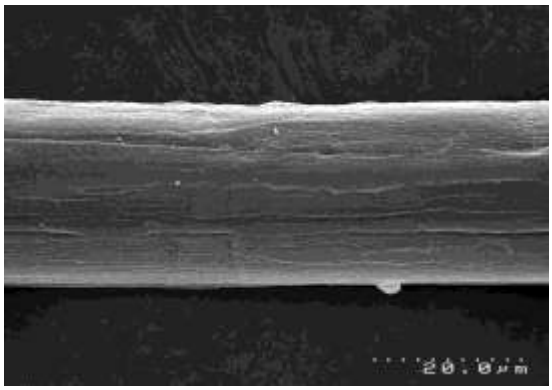


*Figure 1: SEM of untreated hemp fibre*

Alkali treated fibre (see Figure 2a) was seen to have a less glossy surface, indicating removal of noncellulosic compounds, with striations along the fibre length becoming more visible. Treatments with the white rot fungi (D2B, Pyc and S.com) also led to less glossy surfaces (see Figures 2b) and striations becoming more visible along the fibre length.

a



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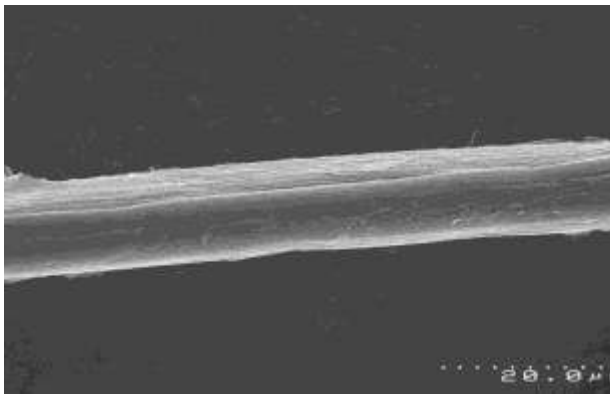

*Figure 2: SEM micrographs of fibre treated with a) alkali, b) D2B fungi*

F13 and B101 treated fibre remained relatively glossy suggesting retention of lignin and non-cellulosics, however, deeper striations were seen to have developed. Combined alkali and D2B treated fibre appeared more striated than for alkali treated only fibre. An extra feature observed for D2B treated fibres were pits in the surface of the fibre, believed to be where fungal hyphae had grown (see Figure 3).

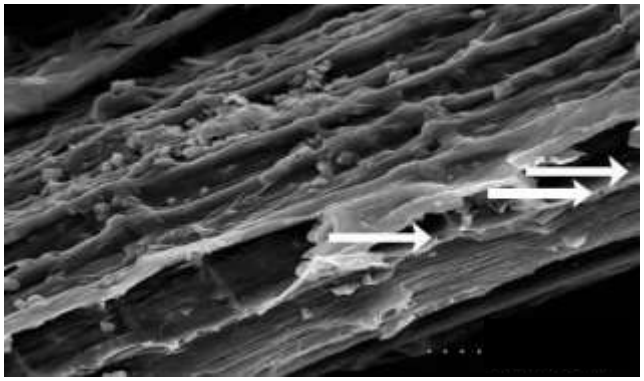

*Figure 3: D2B treated fibre*

## Lignin Testing

A summary of the lignin analysis is given in Table 2. Alkali treatment was found to be the most effective single treatment for lignin removal, however, treatment with D2B was also found to reduce the amount of lignin present compared to the untreated fibre. The expense of analysis limited further quantitative assessment, however, evidence of lignin removal could also be obtained by the change of fibre colour observed with treatment. S.com and Pyc treated fibres were lighter in colour than the untreated fibre, suggesting lignin removal as could be expected for white rot fungi. F13 treatment was expected to remove pitch compounds and B101 expected to remove lignin as detailed in the Introduction, but B101 and F13 treated fibres retained a dark colour similar to the untreated fibre. The combined alkali and D2B treated fibre can be assumed to have the same or less lignin than the alkali treated fibre.

*Table 2: Summary of lignin assessment*

| Treatment | Total lignin (%w/w) | Colour of fibre | Material removed |
|---|---|---|---|
| Untreated | 4.8 | dark | control |
| Alkali treated | 2.1 | light | lignin |
| D2B treated | 4.1 | intermediate | lignin |
| Pyc treated | - | intermediate | lignin |
| S.com treated | - | intermediate | lignin |
| B101 treated | - | dark | - |
| F13 treated | - | dark | pitch (suspected) |
| Combined alkali and D2B treated | - | light | lignin |

## X-Ray Diffraction

The X-ray diffraction patterns of untreated and treated hemp fibre are given in Figure 4.

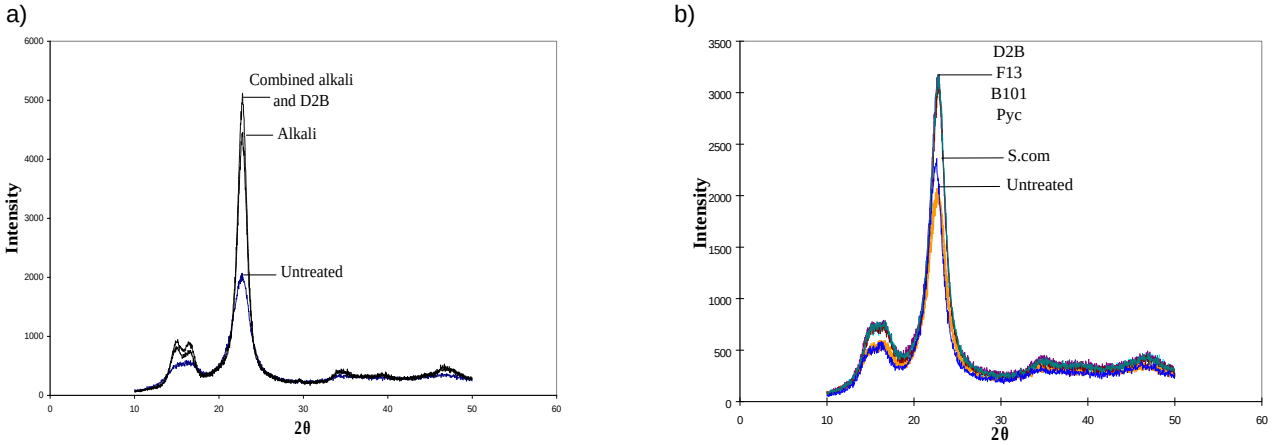


*Figure 4: X-Ray Diffraction Traces for a) untreated, alkali treated and combined alkali and D2B treated fibre, b) untreated and fungal treated fibres(y-axis expanded compared to a)*

The major peaks observed for all fibre samples were at 2θ diffraction angles of 15.1, 16.88 and 22.82$^{o}$ representing $(1\,1\,0)$, (110) (merged in some cases) and (200) planes indicating the presence of Type I cellulose. Table 3 presents a summary of XRD for hemp fibres including crystallinity index calculated according to the Segal empirical method [13]. The crystallinity index was found to increase for all treated fibre, particularly alkali treated fibre and combined alkali and D2B treatment (highest crystallinity index). This could be due to lignin removal, as supported by lignin testing, which would increase overall crystallinity, and allow better packing of cellulose chains which would further increase the degree of crystallinity. For alkali treated fibre and the combined alkali and D2B treated fibre, the two peaks at around 15.1 and 16.88$^{o}$ were seen to be quite separate, unlike the untreated fibre and all the other treated fibre, which further supports lowest amounts of lignin, hemicelluloses, and amorphous cellulose. The crystallinity index increases for all the fungal treated fibre were less than those including alkali treatment, with the two peaks around 15.1 and 16.88$^{o}$ seen to be merged, supporting the removal of lower amounts of lignin and hemicellulose in the case of the white rot fungi, B101 (Zygomycetes), and pitch (resin extractives) in the case of F13 (Ascomycetes).

*Table 3: Summary of X-ray diffraction results*

| Fibres | Appearance of peaks at 15.1 and 16.88$^{o}$ | Crystallinity index (%) |
|---|---|---|
| Untreated | merged | 84.12 |
| Alkali treated | separate | 93.26 |
| D2B treated | merged | 86.78 |
| Pyc treated | merged | 87.08 |
| S.com treated | merged | 87.13 |
| B101 treated | merged | 87.05 |
| F13 treated | merged | 87.69 |
| Combined alkali and D2B | separate | 93.84 |

## Thermal Analysis

DTA curves showed one broad endotherm (around 60°C) and three exothermic peaks (2 merged at the upper temperature end) at higher temperatures, as seen for untreated fibre in Figure 5. The initial temperature of the first exothermic peak represents where the fibres begin to decompose for which a summary is given in Table 4. The untreated hemp fibre started to degrade at about 287°C, however, this value increased for all of the treated fibre, except in the case of S.com where it remained approximately the same, suggesting an increase in thermal stability for the treated fibres, likely to be due to removal of amorphous cellulose or non-cellulosic material. The combined alkali and D2B treated fibre had the highest initial temperature of decomposition (327°C), as would be expected from their high degree of crystallinity and low lignin content.

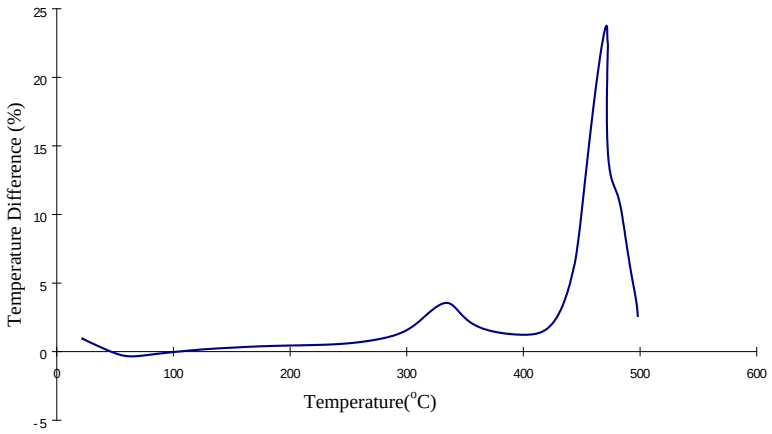


*Figure 5: DTA curve of untreated fibre*

*Table 4: Summary of Thermal Analysis*

| Fibre Treatment | Initial temperature of decomposition (°C) | Activation Energy (kJ/mol) |
|---|---|---|
| Untreated | 287 | 120.43 |
| Alkali | 318 | 157.70 |
| D2B | 314 | 138.17 |
| Pyc | 310 | 127.99 |
| S.com | 289 | 133.87 |
| B101 | 302 | 128.03 |
| F13 | 306 | 124.03 |
| Combined alkali and D2B | 327 | 173.41 |

TGA curves for these fibres showed three important areas of weight loss, as shown in Figure 6 for untreated fibre, relating to the exothermic reactions observed with DTA. The activation energy was calculated for the second exothermic reaction, the main fibre degradation step [14] by the Broido method [15] (summarised in Table 4). The activation energy of untreated fibres was 120 kJ/mol, which increased for all treated fibres up to 158 kJ/mol for alkali treated fibre followed by 173 kJ/mol for fibre with the combined alkali and D2B treatment. The improved thermal stability for treated fibre was believed to be due to reduced non-cellulosic material and increased crystallinity.

## Single Fibre Tensile Strength

The effect of treatment on fibre strength can be seen in Figure 7. The tensile strengths of all treated fibres were reduced by treatment, in some cases, such as alkali, F13, D2B and combined alkali with D2B only slightly, up to around a 50% reduction for S.com. Previous work

improved fibre strength using alkali treatment [1] due to improved packing of crystalline chains. This was evidenced in the current work by the increased crystallinity index, suggesting that for the alkali treatment used here, too much lignin, pectin and hemicellulose, which provides a degree of structural integrity, may have been removed. Less lignin was found to be removed for D2B fibre, with similar expected based on colour change for the other white rot fungi. Fibre strength reduction in these cases could be due to cellulose degradation during treatment, although, neither the XRD, or thermal analysis results support this occurring to a measurable degree. A more likely explanation is that the increased surface roughness, including striations and the presence of holes as seen for fungal treatment gave rise to increased stress concentration and therefore lowered fibre strength.

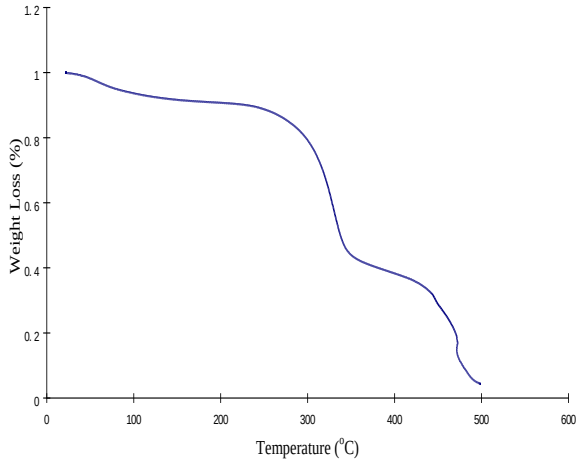


*Figure 6: TGA curve of untreated fibre*

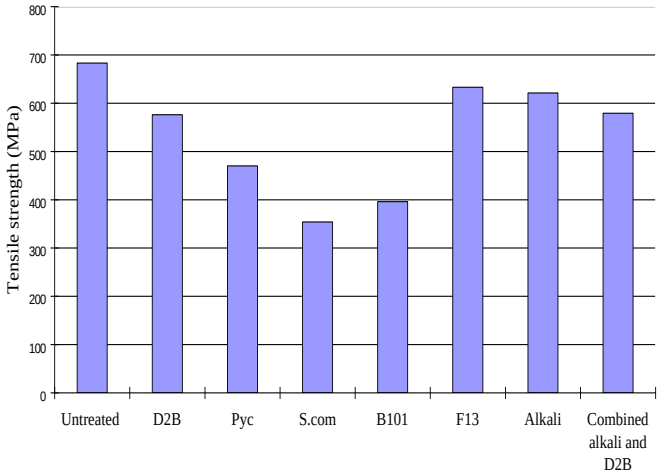


*Figure 7: Single fibre strength*

## Composite Tensile Strength

Composite tensile strength can be seen graphically in Figure 8 and is tabulated in Table 5.

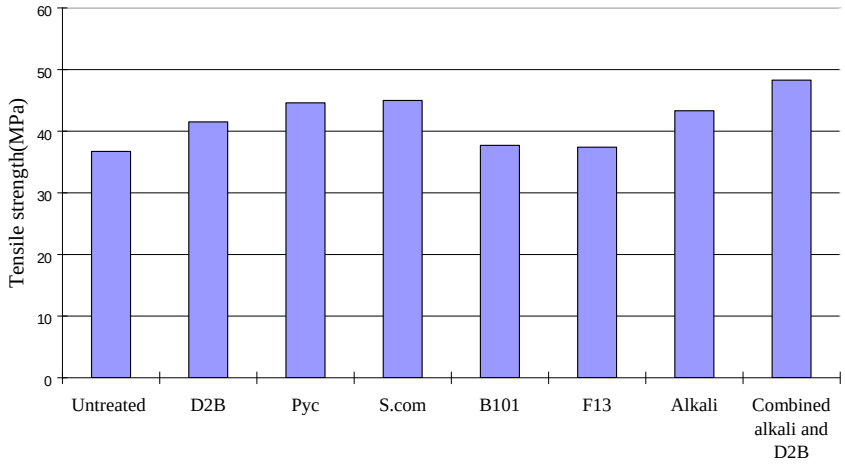


*Figure 8: Tensile strength of untreated and treated fibres composites*

For B101 and F13 treated fibre, there was little change from the untreated fibre composites. For these two fungal treatments, no effect had been observed regarding lignin removal. However, it was suspected that some lignin may have been removed for B101 and some pitch removed for F13, as supported by increased crystallinity index and thermal stability, which along with increased roughness, would be expected to increase hydrophyllicity and increase coupling between MAPP within the polypropylene and the hydroxyl groups on the fibre and explain why composite strength was retained despite a large reduction of fibre strength. Improvement in composite strength was obtained for all the white rot fungi and alkali treatments, as well as for the combined alkali with D2B white rot fungal treatment. The best results by fungal treatment alone were obtained for S.com, which had produced the lowest single fibre strength, suggesting that the interfacial bonding achieved had been greatly improved through removal of lignin (supported by colour change and XRD results), and increased roughness, again enabling increased coupling between MAPP within the polypropylene and the hydroxyl groups on the fibre. The best overall results were obtained using a combined alkali and D2B fungal treatment, despite the alkali treatment alone giving higher fibre strength. This further supports fungal treatment as giving extra benefit in terms of improved fibre morphology, possibly related to the pits produced by hyphae, providing better mechanical interlocking and increased potential for interaction between the hydroxyl sites and the MAPP coupling agent.

*Table 5: Summary of the effect of treatment on composite tensile strength*

| Fibre | Increased surface roughness | Removal of lignin | Fibre tensile strength (MPa) | Composite tensile strength (MPa) |
|---|---|---|---|---|
| Untreated | control | control | 683 | 36.7 |
| D2B treated | yes | yes | 576 | 41.5 |
| Pyc treated | yes | yes | 470 | 44.58 |
| S.com treated | yes | yes | 354 | 44.98 |
| B101 treated | yes | suspected | 396 | 37.7 |
| F13 treated | yes | Unknown (Pitch removal suspected) | 633 | 37.4 |
| Alkali treated | yes | yes | 621 | 43.3 |
| Combined alkali and D2B treated | yes | yes | 579 | 48.28 |

## CONCLUSIONS

Alkali treatment was found to approximately half the lignin content of hemp fibre as well as increase its crystallinity and surface roughness. As a consequence, the thermal stability was found to increase. The resulting composite strength was found to increase by 18% compared to untreated fibre composites despite the small reduction in fibre strength. This was believed to be as a consequence of improved wettability and coupling with MAPP in the matrix as well as the improved mechanical interlocking potential.

Treatment using fungi, including white rot fungi, was found to remove less lignin than alkali treatment. However, despite this, and the fibre strength being reduced quite dramatically in some instances, composite strengths in the majority of cases were found to be better than untreated fibre composites. This has been suggested to be due to improved mechanical interlocking possible with the matrix, including that due to the production of pits in the fibre walls believed to be due to the action fungal hyphae, observed with D2B fungi, enabling good

mechanical keying of the matrix to the fibre. The best results for fungal treatment alone, gave an increase in composite strength of 22% compared to untreated fibre composites, however in combination with alkali treatment gave an overall improvement of 32% along with improved thermal stability. Results show potential for the use of fungal treatment of hemp fibre either alone or in combination with alkali treatment, for improving reinforcement in thermoplastic matrices.

## Acknowledgements

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