

## **EFFECT OF FIBRE TREATMENTS ON MECHANICAL PROPERTIES OF FLAX/TANNIN COMPOSITES**

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### **ABSTRACT**

Due to the inherent environmental benefits of using natural resin (tannin) and natural fibre (flax), flax/tannin composites could be potentially used for vehicle applications. One of the main limitations is the hydrophilic property of flax, resulting in the poor fibre/hydrophobic matrix interface quality. Alkali, acetylation, silane treatment and enzymatic treatment were selected to modify non-woven flax mats to prepare the composites. The fibre morphology was studied through scanning electronic microscopes (SEM). The effects of fibre pre-treatments on dynamic and static mechanical properties of composites were investigated through adequate experiments, such as dynamic mechanical analysis (DMA) and static tensile testing. The modified rougher fibre surface broadened the glass transition peaks of composites due to the improved surface adhesion. However, there is no big improvement of tensile strength after modifications. The pure NaOH (sodium hydroxide) treated composites remain the tensile properties and offer good flax/tannin wettability.

**Keywords:** Flax/tannin, fibre treatments, mechanical properties.

### **1 INTRODUCTION**

Natural fibre-reinforced fully bio-composites have attracted the interest of many industries due to their comparative mechanical properties and outstanding bio-degradability characteristics (Fan *et al.* 2011; Kalia *et al.* 2011). The composite made from tannin and flax fibres could potentially offer desirable characteristics aiming at reducing the environmental footprint of superlight electric vehicles through the use of bio-materials for load-bearing parts such as vehicle body panels, crash elements, side panels and body trims (Zhu *et al.* 2012; Avril *et al.* 2012). However, the incompatibility between hydrophilic flax fibre and hydrophobic tannin resin limits their interphase quality and hence the mechanical properties. Mercerization, acetylation, silane treatment, and other fibre pre-treatments are commonly used for flax composites to solve the problems (Van de Weyenberg *et al.* 2003).

Flax fibres are amendable to chemical modification due to the presence of hydroxyl groups. The hydroxyl groups may be involved in the hydrogen bonding within cellulose molecules, thereby activating these groups or can introduce new moieties that form effective interlocks within the system. The interfacial properties can be improved by giving appropriate modifications to the components, which give rise to changes in physical and chemical interactions at the interface.

The suitable treatment on flax fibres may improve the mechanical performances of the final composite mechanical performances. Alkali treatment of natural fibres, also called mercerization, is

the common method to produce high-quality fibres. From the recent investigation, it is the alkali concentration that mainly controls the extent of mercerization, influencing the molecular compositions. The sufficient alkali concentration for the treatment is 5-10% NaOH for hours followed by rinsing and drying. Acetylation is a well-known esterification method originally applied to wood cellulose to stabilize the cell walls against moisture, improving dimensional stability. Coupling agents usually improve the degree of crosslinking in the interface region and offer a perfect bonding. Xie *et al.* (2010) have reviewed silane coupling agent modification to natural fibre composites and found out improvements in strength, moisture absorption and fungal resistance for epoxy composites. The suitable silane modification for fibres in epoxy composites was aminopropyl triethoxy siloxane (APS) and for methacryloxypropyl trimethoxysilane (MPS). Enzymes are an increasingly interesting option as such or when combined with chemical and mechanical methods for modification and processing of biomaterials. The laccase-catalysed modification can be used to tailor the properties of various lignocellulosic materials, including flax fibre materials based on the application needs (Kim and Cavaco-Paulo 2012). Lauryl gallate, a hydrophobic compound with strongest internal sizing effect, were grafted on cellulosic fibres, and the results showed significant reduction of water penetration (Garcia-Ubasart *et al.* 2012; Garcia-Ubasart *et al.* 2011).

In authors' study, flax fibres with five different surface treatments were firstly applied with tannin resins. The mechanical properties of the final composites were investigated through DMA and tensile tests. In order to understand the treatment effects, the fibres surface were also examined through SEM.

## 2 MATERIALS AND EXPERIEMENTS

### 2.1 Materials

Non-woven flax fibre mats with different surface treatments were supplied by Valtion Teknillinen Tutkinuskesku (VTT). The mercerization was made by immersing the flax mats into 5 w-% NaOH solution for two hours, washing them two times thoroughly with water and drying in 50°C for 12 h. This NaOH treatment was made as pre-treatment also for butanetetracarboxylic acid (BTCA) and amiopropyltriethoxysilane (APS) treated mats. The BTCA treatment was done by spraying 1% BTCA-water solution on both mat surfaces to an amount respecting 5% of BTCA on fibres. APS treatment was made for moist mats by spraying 1% APS in ethanol-water solution (80:20) on both mat surfaces. Treated and untreated non-woven flax mat reinforced tannin composites manufactured by compression moulding were provided by University of Lorraine-ENSTIB (Table 1). Two mat layers were used in each composite to obtain 50 wt% of fibre/resin ratio.

Table 1: Investigated flax composites and associated flax mats.

Composite type	Treatment method	Studied fibre mat
T	None	Yes
1	5% NaOH	Yes
2	NaOH+BTCA	Yes
3	NaOH+APS	Yes
4	Laccase	No
5	Laccase-Doga (LD)	Yes

\* BTCA- Butanetetracarboxylic acid, APS- Amiopropyltriethoxysilane, Laccase-Benzenediol, Doga-dodecyl gallate.

### 2.2 Characterisation and tests

#### 2.2.1 Scanning Electron Microscopy (SEM)

Fibres were extracted from the treated and untreated flax mats, and then were examined using a XL30 SFEG analytical high resolution scanning electron microscopy (SEM), supplied by FEI.

### 2.2.2 Dynamic mechanical analysis (DMA)

Each composite specimen of 35×12 mm was placed in a Thermal Analysis Instruments Q800 DMA using single cantilever bending mode and liquid nitrogen cooling system. The temperature was heated from room temperature to 200°C at a heating rate of 3°C/min and a frequency of 1 Hz.

### 2.2.3 Quasi-static tensile testing

Tensile tests (at least three specimens each group) according to ASTM 3039 were carried out using a universal Instron 500/100 machine with the head speed of 2 mm/min. The gauge length was 150 mm. Digital image correlation (DIC) method were used for micro-strain investigation.

## 3 RESULTS AND DISCUSSION

### 3.1 Fibre surface morphology

The SEM clearly shows differences in the surface morphology of the flax fibres depending on the applied fibre surface modifications, including 5% NaOH, BTCA, APS and Laccase-Doga (LD). Figure 1 provides details about the surface characteristics of flax fibres with and without chemical treatments.

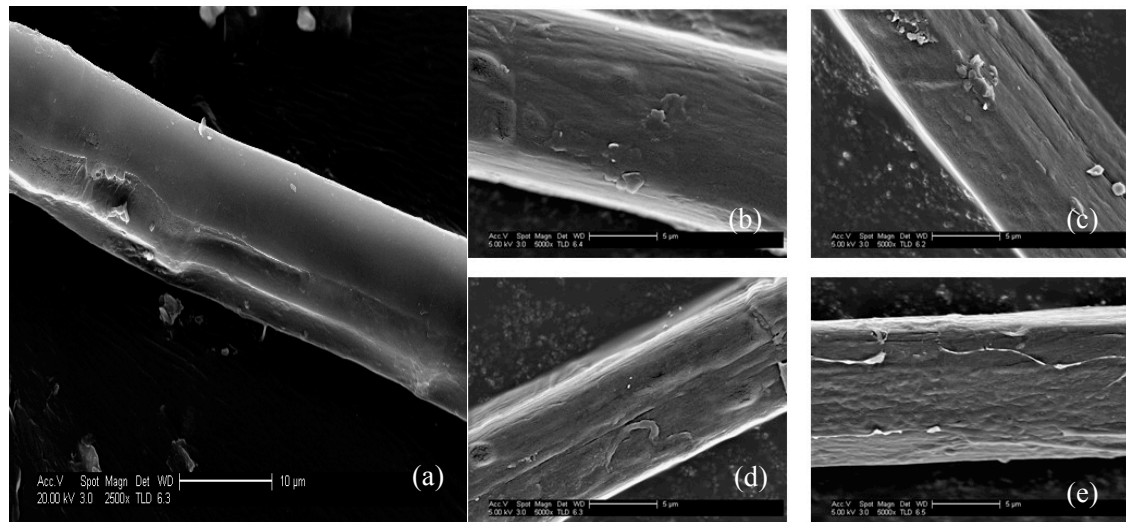


Figure 1: SEM morphologies of flax fibres: (a) untreated; (b) NaOH; (c) NaOH-BTCA; (d) NaOH-APS; (e) Laccase-Doga.

From Figure 1(a), the untreated fibre structure was not clear and partially covered by attached smooth substances, such as fibre waxes and fats. A very effective procedure to purify the flax fibres is alkalization using NaOH, resulting in the removal of waxy, the primary cell wall and other additives. It can be seen from Figure 1(b) that the resultant fibre surfaces were more structured with obvious striations as the lamella ordered by flax fibre fibril. The clear cut difference in the surface morphology is due to the dissolution of lignin, hemicellulose, and waxy materials which increases the inter-fibrillar region and imparts a rough texture to surface (Yan *et al.* 2012). The knuckle-swellings and disclamination as present in the raw fibres can still be found after NaOH-treatment. It is reported that the higher NaOH concentration (10%) may start the conversion of the crystalline form from cellulose I to cellulose II, which causes deeper and broader striation (Yan *et al.* 2012). The surface features of fibres were also clearly visible for other three modifications (BTCA, APS and LD). In addition, more structure of raw fibre cell wall on the three treatments was exposed on the fibre surface than that of the NaOH-treated flax fibre. Another thing noted for LD fibre was the thin layer with many small protrusions, which were considered as the grafted hydrophobic Doga compounds. In conclusion, the rougher fibre surfaces have the potential to improve the fibre/matrix adhesion.

### 3.2 Effect of treatment on dynamic mechanical properties of composites

Dynamic mechanical analysis done in the experiments studied the effect of fibre surface treatments on the temperature dependency of viscoelastic properties of flax/tannin composites. Figure 2 shows the testing curves corresponding to storage and loss modulus-. transition temperatures (shown in Table 2) were determined based on these figures.

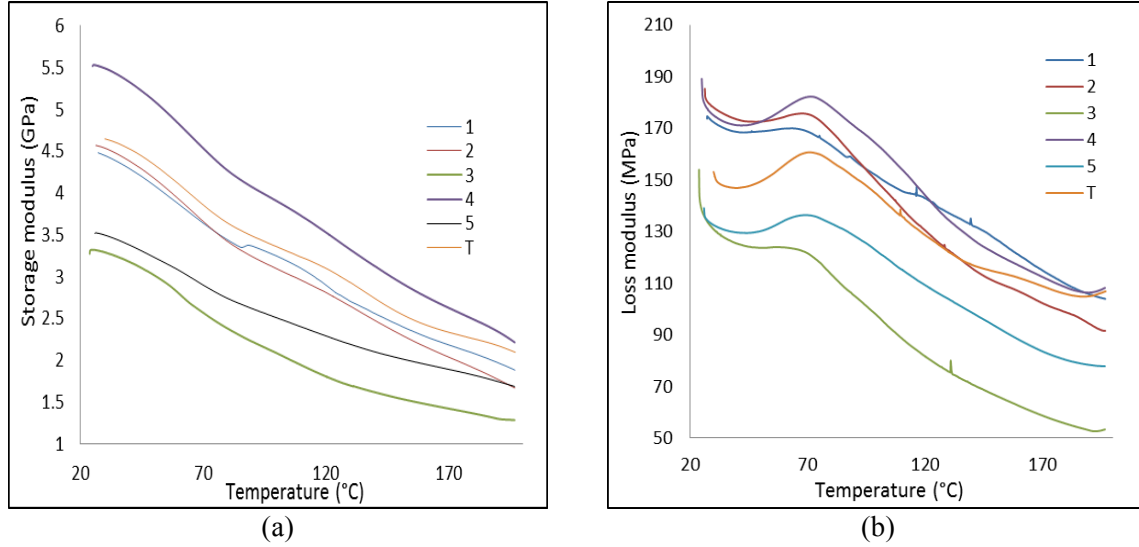


Figure 2: DMA curves : (a) storage modulus-temperature; (b) loss modulus-temperature.

Table 2: Part of the obtained DMA quantitative values,

Types	E' at 27°C (GPa)	E'' at 27°C (MPa)	T <sub>g</sub> (loss modulus) (°C)
1	4.4	174	63
2	4.5	181	67
3	3.3	134	64
4	5.5	178	70
5	3.5	135	69
T	4.6	153	71

For composites, storage modulus directly refers to the elastic characteristic highly influenced by the fibre/matrix adhesion. From Figure 2(a), the initial storage modulus of composites at 27°C varied quite a lot as a result of different fibre treatment techniques employed. The type 4 composite showed higher storage modulus of 5.5 GPa, compared with the storage modulus (4.6 GPa) of type T (unmodified) composite. Clearly, Laccase treatment for type 4 has a significant positive effect on the interfacial bonding due to the rougher fibre surface topography after partially or completely removing the non-cellulose lignin during processing. Except for type 4, the other modified composites including type 1, 2, 3 and 5 exhibited lower storage modulus at 27°C than the type T composites. The complex structure of flax fibres makes it difficult to give a precise and accurate explanation for the resultant variation in initial storage modulus. The rougher fibre enlarges the fibre/matrix contact surface, improving the load transfer, while the rearranged or re-oriented fibrils would lead to a better stress/load carrying ability along the fibre axis; also the reduced fibre length/diameter ratio allows the fibre reinforcement more efficiency. However, the stress transfer between fibrils could possibly decrease by weakening the interfibrillar matrix materials, such as lignin and hemicellulose, leading to loss of storage modulus.

The most important transition temperature obtained from DMA analysis is the glass transition temperature ( $T_g$ ), which could be read from loss modulus curves. Loss modulus represents the viscous portion of materials and reaches a maximum value at the glass transition. This  $T_g$  is reported to be more reliable because the  $T_g$  obtained at the  $\tan\delta$  peak overestimates glass transition temperature. The  $T_g$  of type T (unmodified composite) was found at around 71°C, while the other  $T_g$  were in the range

from 60 to 70 °C. The similarity of  $T_g$  reveals that the surface treatments have little change on the overall mobility of tannin resins. Some unusual small sharp peaks occurred in both loss modulus of type 1, type 3 and type T composites. The reason has not been determined but possibly is the post-cure of tannin resins or other cross-linking reactions. Compared to the type T composite, a significant change in the treated-flax fibre composites is the broadening of the  $T_g$  peaks, attributed to the improved internal adhesion increasing the modulus gradient of tannin resins. The resin layer on the fibre surface showed higher modulus than the rest.

### 3.3 Effect of treatments on tensile properties of composites

The effects of fibre surface modifications on tensile behaviour of flax/tannin composites were studied. The possible changes in flax/matrix adhesion is factor for mechanical performances of composites after fibre treatments. The tensile strength and modulus of flax/tannin composites are summarized and showed in Figure 3.

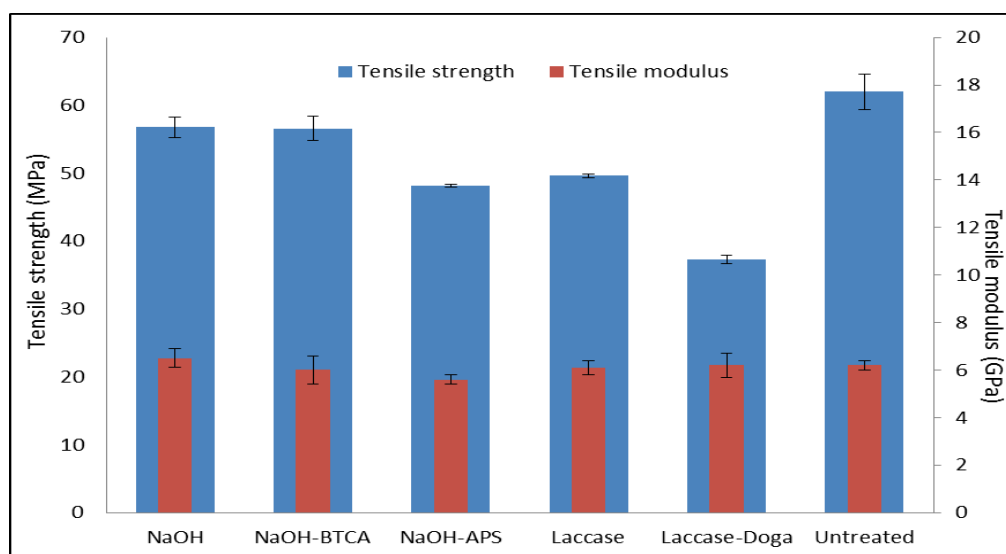


Figure 3: Tensile strength and modulus of flax/composites with treatments.

As seen in Figure 3, the performance of composites with 5% NaOH (type 1) and NaOH-BTCA (type 2) treatment (tensile strength of around 58 MPa) was comparable to the original composite (type T). All other treatments lowered the tensile strength of the composite. This strength reduction is possibly related to the loss of intra-matrix (e.g. hemicellulose) between micro-fibrils during surface treatments. From the distribution of tensile strength in Figure 3, the NaOH-APS, laccase and LG-D treated composites showed much smaller variation than the neat fibre composites. The tensile properties of the composites hence are more stable and consistent. In terms of the modulus, the NaOH-APS treated flax composites showed the smallest tensile modulus of 5.6 GPa, around 10% less than that for untreated composites (6.2 GPa). Singha and Rana (2012) have reported that the APS treatment will destroy packing of the cellulose chains to a certain extent and causes disorder in the crystalline pattern of the main polymeric backbone. Other surface treatment methods like NaOH, NaOH-BTCA, Laccase, and Laccase-Doga had little effect on the tensile modulus of fabricated composites. It indicates that these surface treatments only influence the re-arrangement of micro-fibrils by transferred stress towards the tension direction, after the initial linear stress-strain part. This may be due to the loss of intra-fibril matrix, making the extension of micro-fibrils more easily.

## 4 CONCLUSIONS

Five fibre pre-treatments were employed and expected to enhance the mechanical performances of flax/tannin composites. The roughness of the fibre surface clearly increased after the treatments through the SEM images. It may ideally benefit the fibre/matrix adhesion and the mechanical properties. However, the DMA results showed the broadened  $T_g$  peaks and complicated initial storage

modulus, while reduction of tensile strength was observed after some modifications. NaOH and NaOH-BTCA treated composites maintain the tensile properties. The two methods are more compatible with tannin system and offer good flax/tannin wettability. In addition, NaOH-APS, laccase and LG-D treatments result in more consistency of the tensile properties of the composites.

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