

# HYGROEXPANSION OF WOOD-FIBRE COMPOSITE MATERIALS: EFFECTS OF CELL-WALL CROSS-LINKING AND COMPOSITION OF THERMOPLASTIC MATRIX

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## ABSTRACT

Effects of BTCA (Butantetracarboxylic acid) modification, choice of matrix and fibre fraction on hygroexpansion of wood-fibre composites were investigated. Untreated reference softwood fibres and BTCA modified fibres were used in wood-fibre composites where PLA (Polylactic acid), PP (Polypropylene) or a mixture of the two were used as matrix. The BTCA modification reduced the out-of-plane hygroexpansion of PLA and PLA/PP composites, while the swelling was increased when PP was used as matrix material. This is explained by difficulties to adhere the BTCA modified fibres to PP matrix during manufacturing of the composites. Fibre fraction was the most important parameter to out-of-plane hygroexpansion, high fibre fraction leading to large out-of-plane hygroexpansion.

## 1. INTRODUCTION

Rising oil prices and increased environmental awareness have contributed to the advance of research and development of natural-fibre composites, where natural fibres, such as hemp, flax and wood fibres, are used as reinforcement in a polymeric matrix. Natural fibres are derived from a renewable resource and are biodegradable, have high specific stiffness and strength and low density [1, 2]. The absorption of water and moisture, causing swelling and deformation of the fibres, does however prevent natural fibres from reaching their full potential as reinforcing material. Several methods to reduce swelling of natural-fibre composites have been investigated under the years. Acetylation has proved to reduce swelling of natural-fibre composites, but stiffness and strength have been reported to decrease when acetylation is used [3-7]. This drawback can however be avoided if certain types of matrix systems are used, according to Gomez-Bueso et al [8]. Steaming has been reported to give similar effects, with reduced swelling, stiffness and strength [4,9]. Methods using cross-linking reactions have been used to improve the dimensional stability of wood [10] and paper [11]. In this work cross-linking with BTCA (Butantetracarboxylic acid) [12-13] was used to restraint wood fibre swelling and to provide a higher degree of dimension stability of cellulose fibres.

To study the effect of BTCA modification on hygroexpansion and diffusion of wood-fibre composites, tests under humid and immersed conditions were performed. The tests were evaluated by measurements of the change in dimensions and weight increase due to absorption of moisture and water. The coefficient of diffusion was determined with Fick's law. Mechanical properties and microstructure of the composite samples was studied through three point bending tests and scanning electron microscopy, respectively. To investigate the role of matrix material to hygroexpansion and diffusion of the composite material two different thermoplastic matrix materials were used, PLA (Polylactic acid) and PP (Polypropylene). Influence of fibre fraction was also investigated.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Bleached birch kraft fibres from industrial pulp were used. Part of the fibres underwent a cross-linking reaction with BTCA in order to increase their resistance to water and moisture. Both the BTCA modified fibres and the untreated reference fibres were used for composite manufacturing. The polymers used as matrix material were PLA (Unitika Sample) and PP (Baumhueter extrusion GmbH). PLA is a thermoplastic polyester manufactured from renewable resources like corn, sugar beets, wheat and other starch-rich products [2, 14]. The high stiffness and strength, the biocompatibility and biodegradability have made it to a commercially interesting material. PLA has been used in previous studies of wood fibre composites with promising results [15-16]. PP is an inexpensive commodity thermoplastic and is commonly used when making natural-fibre composites for commercially available applications, such as extruded boards for flooring and decking. PP has lower strength and stiffness compared to PLA and is more ductile than the rather brittle PLA [15]. A mixture of PLA and PP (50 weight % of each) was also used as matrix material, i.e. three types of matrix systems were used, PLA, PP and the mixture of the two. The influence of fibre fraction was investigated as well. A total of 24 different types of composites were manufactured, Table 1. Wood-fibre mats of reference and BTCA modified fibres were produced to further evaluate the effect of BTCA modification.

Table 1: Combinations of constituents in composite materials

Composite sheets		Weight percentage wood fibres				
Polymer	Wood fibres	100%	70%	60%	40%	30%
PLA	Reference	•	•	•	•	•
PLA	BTCA modified	•	•	•	•	•
PP	Reference		•	•	•	•
PP	BTCA modified		•	•	•	•
PLA-PP	Reference		•	•	•	•
PLA-PP	BTCA modified		•	•	•	•

### 2.2 BTCA modification

Fibres were mixed with water at 2000 revolutions (rotational frequency of the mixing propeller was approximately  $49 \text{ s}^{-1}$  according to ISO 5263-1:2004) with a consistency of 3% (w/w). The pulp was washed once with deionised water and thereafter put in 0.02 M NaOH over night for pre-swelling. The pulp was then washed three times with deionised water to remove the NaOH. The fibres were thereafter treated with a water solution containing 2% BTCA and 2% NaHPO<sub>4</sub> for 1 h in 1 atm and 1.25 h in vacuum. The solution was then removed by filtration and the pulp was dried at room temperature. The fibres were cured 15 min at 150°C. To remove excess BTCA and reduce fibre agglomeration the pulp was soaked, washed and beaten repeatedly and there after dried at room temperature [17].

### 2.3 Manufacturing of composites and test specimens

Wood fibres were mixed with PLA fibres, PP fibres or with an equal mixture of the two. Wood and plastic fibre sheets were formed on a regular sheet former rendering in-plane random orientation of the fibres and a basis weight of  $200 \text{ g/m}^2$ . To obtain thicker

specimens 20 sheets were stacked and pre-heated in an oven 20 minutes at 190°C before being hot pressed at 120°C and 400bar during 2 minutes.

Flat circular test specimens with a diameter of 50 mm were machined from the produced composite plates. The thickness of the samples was approximately 4 mm. A number of the circular specimens were partially delaminated after the milling operation. This separation in the out-of-plane direction is explained by incomplete melting of the polymer fibres in the centre of the composite specimen and incomplete fibre wetting of high fibre fraction composites. To recover the original shape and obtain fully melted specimens, an additional pressing was carried out. After pre-heating the samples 15 min at 190°C samples were pressed again during 2 min with a hydraulic pressure of 100 bar. The specimen edges were polished to gain smooth cross sections.

#### **2.4 Water Retention Value**

The treated fibres were evaluated against the reference fibres by determining the water retention value (WRV) according to standard SCAN-C 62:00. The water retention value is the ratio of wet fibre mass after excess water on surfaces and inside lumen has been removed and dry fibre mass. The wet fibre mass was obtained by centrifuging 50 mg soaked fibres at, 5010 rpm for 15 min. The water left after centrifugation is correlated to water inside the fibre cell wall. The fibres were then dried at 105°C for 2 h to obtain the dry weight.

#### **2.5 Sorption and swelling test, under humid conditions and water immersion**

In order to obtain dry reference weight and dimensions of the specimens, samples were dried in an oven for 72 h at 50 °C. After the conditioning, the specimens were directly weighed and dried further. They were weighed again after 48 h to confirm that dry conditions had been reached. Tests under humid conditions were carried out in a sealed test chamber with a relative humidity of 97%. The salt Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O was used to maintain the relative humidity during the test. Water soaking tests were performed according to standard ASTM D 570-81. The specimens were placed inside plastic containers filled with water maintained at 23°C. Before measurements the specimens were taken out from the water filled containers and visible surface liquid was carefully removed with a paper cloth. The measuring times were short compared to the total test period (90 days) and the time out of the test chamber or water should therefore not significantly affect the result [18-19].

All specimens were marked with five points for thickness measurements and six points for radial readings. Measurements of thickness were performed with a digital micrometer (NSK 0-25 mm) with 1 µm precision. Diameter readings were performed with a digital vernier calliper (BDC150X 0-150 mm), precision of 0.01 mm and weight was determined with analytical balance scale (Mettler AE 163), precision of 0.1 mg. Readings were made at increasing intervals, starting with hourly intervals and later daily and weekly measurements.

#### **2.5 Microscopy survey**

Small samples of composite material were imbedded in epoxy and smooth cross sections were polished. The electron microscope used was a Philips XL30 ESEM-FEG (Environmental Scanning Electron Microscope-Field Emission Gun). The working conditions were low vacuum mode, BSE detector, 0.6 Torr pressure in sample chamber, 15 kV acceleration voltage and working distance approximately 7-8 mm.

## 2.6 Coefficient of diffusion

Fick's second law of diffusion [20] was used to determine the coefficient of diffusion,  $D$ , for the composite samples. Espert et al. [21] showed that water absorption in natural-fibres/PP composites followed the kinetics of a Fickian diffusion process. The weight gain of the sample as a function of time and location in the sample is described by

$$w(t) = w_0 + (w_\infty - w_0)G(t) \quad (1)$$

where  $t$  is time, the initial weight gain of the sample is  $w_0$  and  $w_\infty$  is the weight gain of the moisture saturated sample. When  $t$  approaches infinity, the weight gain of the sample,  $w(t)$ , approach  $w_\infty$  everywhere in the material. The initial condition is  $w(0) = w_0 = 0$  assuming dry specimen at the beginning of the measurement. For one-dimensional diffusion the function  $G(t)$  is given by [18]

$$G(t) = 1 - \frac{8}{\pi^2} \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} \exp[-(2k+1)^2 \pi^2 t^*] \quad (2)$$

where

$$t^* = \frac{Dt}{h^2} \quad (3)$$

and  $h$  is the thickness of the sample. Equation (2) was adjusted to fit experimentally determined data using 50 terms in the summation and the coefficient of diffusion was hence determined.

## 3. RESULTS AND DISCUSSION

### 3.1 Water retention value

A water retention value (WRV) test was performed on BTCA modified and reference fibres before manufacturing of the composites. Wood fibre mats of modified and reference fibres were also tested under humid conditions together with the composites. The results show a significant reduction of WRV and moisture absorption for BTCA treated fibres. The WRV show a decrease from 1.6 for reference fibres to 0.5 for BTCA modified fibres. The results for the vapour sorption test show the same trend. The weight gain was 27% for reference fibres and 18% for BTCA treated fibres after 90 days in 97% relative humidity, respectively. These results suggest that the BTCA treatment was successful.

### 3.2 Diffusion and hygroexpansion

Thickness and weight increase were determined continuously during 90 days to investigate the effect of the BTCA modification, matrix composition and fibre content on hygroexpansion and diffusion of wood-fibre composite materials. Figure 1a shows the weight increase of composites tested under humid conditions when PLA was used as matrix material. There is a significant difference between reference-fibre and BTCA-fibre composites. The diffusion (i.e. the slope of the curve in Figure 1a) of composites with BTCA modified fibres is slower than results for reference-fibre composites. This is significant for high fibre contents where the swelling rate is high. Reference-fibre

composites absorb more moisture than composites where BTCA modified fibres are used. For composites tested under humid conditions and with PP as matrix material the

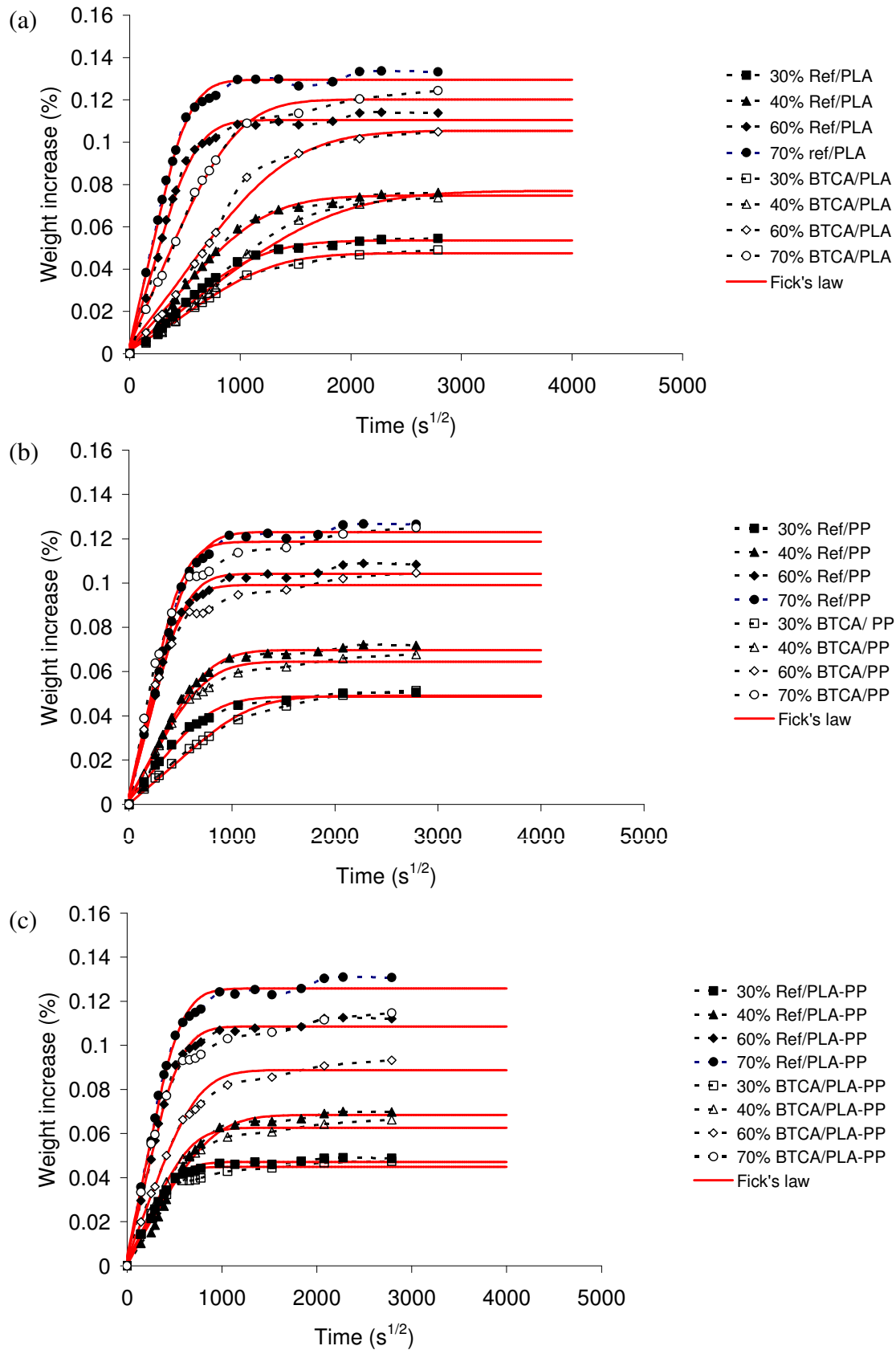


Figure 1: Weight increase and diffusion behaviour of composites with reference and BTCA modified fibres. Matrix material is (a) PLA, (b) PP and (c) PLA-PP mixture.

trend is not as clear as that for composites where PLA matrix is used. The moisture content at saturation is reduced but no difference in diffusion rate is seen, Figure 1b. The specimens containing matrix of 50% PLA and 50% PP shows similar results as PLA composites, with decreased moisture absorption at saturation and low swelling rates for composites with high fibre contents, see Figure 1c.

Coefficients of diffusion determined with curve fitting to Fick's law of diffusion for composites tested under humid conditions are tabulated in Table 2. The  $R^2$  value is a measure of how well the predicted diffusion fits the experimentally determined data, a perfect fit corresponds to a  $R^2$  value equal to 1. As seen in Table 2, where  $R^2$  values are presented in parenthesis for each predicted coefficient of diffusion, the predicted data offer good agreement to the experimentally determined data.

Table 2: Coefficient of diffusion for the composite materials tested under humid and wet conditions,  $R^2$  values in gray.

Composite		D ( $10^{-6}$ mm <sup>2</sup> /s)			
Matrix	Wood fibres	Weight percentage wood fibres			
		30%	40%	60%	70%
PLA	Reference	1.5 (0.91)	1.2 (0.92)	5.8 (0.94)	6.8 (0.97)
PLA	BTCA modified	0.56 (0.97)	0.52 (0.88)	0.86 (0.90)	2.4 (0.95)
PP	Reference	3.3 (1.00)	3.4 (0.92)	7.7 (0.99)	5.8 (0.96)
PP	BTCA modified	1.5 (1.00)	4.4 (0.97)	1.1 (0.98)	9.0 (0.98)
PLA/PP	Reference	7.5 (0.97)	2.2 (0.89)	7.1 (0.95)	6.9 (0.97)
PLA/PP	BTCA modified	7.1 (0.99)	3.0 (0.98)	3.6 (0.97)	6.8 (0.98)

Out-of-plane hygroexpansion for composite materials tested under humid and wet conditions are presented in Figure 2. When PLA is used as matrix material a significant difference between reference-fibre and BTCA-fibre composites is seen. The hygroexpansion of composites with 60% and 70% BTCA modified fibres is approximately one third of the results for reference-fibre composites. The hygroexpansion increased with increasing fibre fraction. Reference-fibre composites reached thickness saturation about ten days earlier than composites with same dimensions where BTCA modified fibres are used. For composites with PP as matrix material the trend is opposite to that of composites where PLA matrix is used. The BTCA modified fibres increase, or have little effect, on the out-of-plane hygroexpansion. The increased swelling may be explained by processing difficulties, with fibre aggregates and poor wettability (especially for high fibre contents) inevitably leading to a poorly consolidated material containing cracks and voids. The compatibility problem of hydrophilic cellulose based fibres and hydrophobic matrix materials such as PP is a well-known challenge, and several chemical techniques have been investigated to improve the interfacial bonding [22]. The specimens containing matrix of 50% PLA and 50% PP shows similar results as PLA composites. The BTCA treatment shows positive results in all PLA-PP composites, and most noticeable for 60-70% fibre content (see Figure 1c). The sample 70% reference fibres and PP was not soaked in water since the quality of this sample was too poor. Soaking of the sample would lead to rapid dispersion after only a short period of time, making results uncertain. The BTCA treatment shows positive results in all PLA-PP composites most noticeable for 60-70% fibre content.

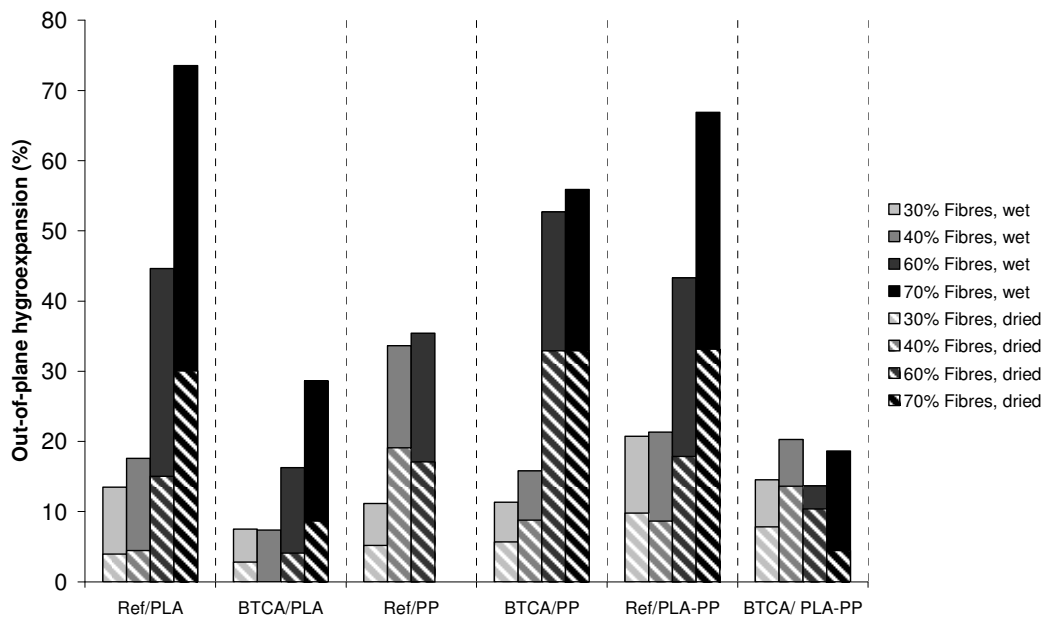


Figure 2: Out-of-plane hygroexpansion for composites tested under wet (single colour) and humid (striped) conditions

### 3.3 Redrying

The combination of BTCA modified fibres and PP shows the highest remaining thickness change when samples were dried after the saturation in humid environment. This could suggest that the interface in PP/BTCA composites is weak and permanently destroyed by moisture or by the moisture induced swelling. For the combination of BTCA modified fibres and PLA an increase of only a few percent remains after drying, Figure 3.

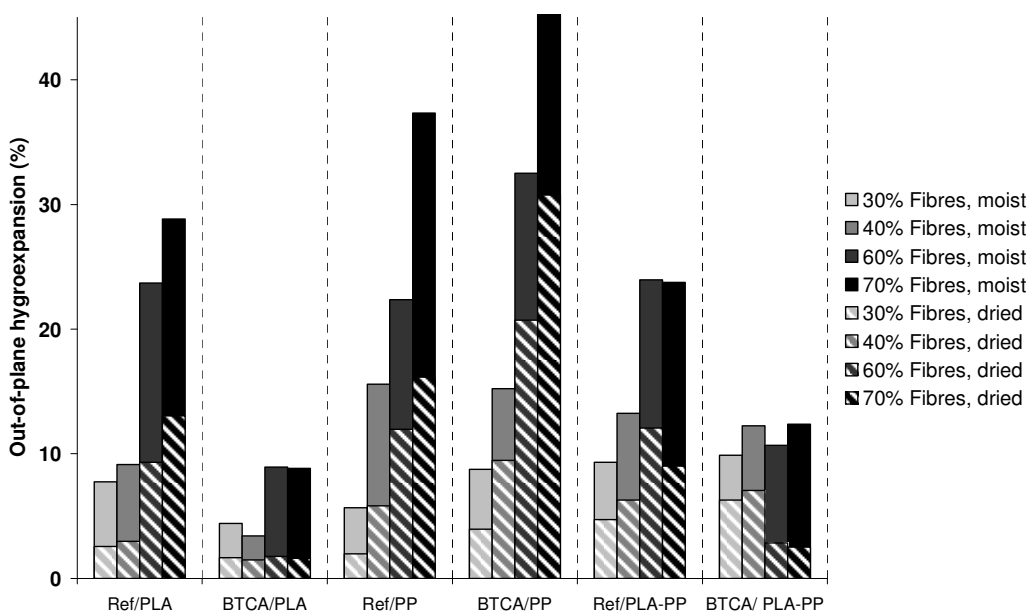


Figure 3: Remaining thickness change after drying of moisture saturated samples

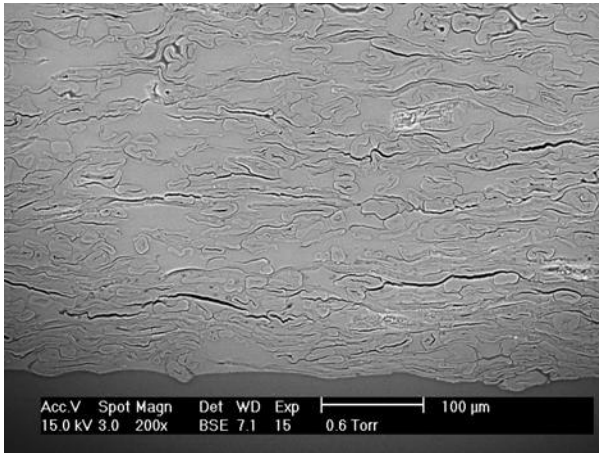


Figure 4a: Micrograph of PLA composite with 60% reference fibres. The fibre network is dense and the wettability is good.

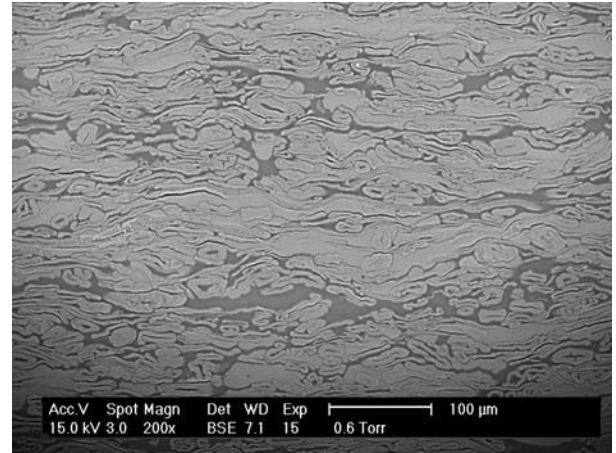


Figure 4b: Micrograph of PLA composite with 70% reference fibres. The dark regions are air pockets.

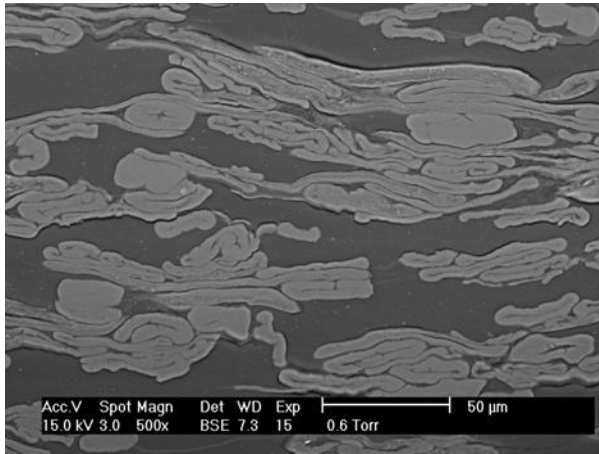


Figure 4c: Micrograph of PP (dark grey) composite with 40% reference fibres (light grey). Compact composite with contact between fibres.

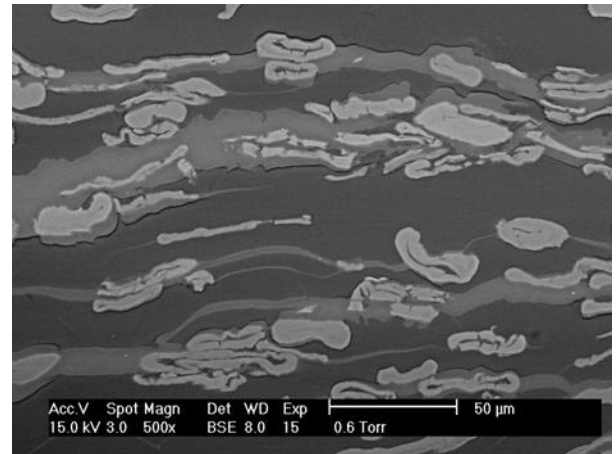


Figure 4d: Micrograph of PP composite with 40% BTCA fibres. Poor dispersion of (light grey) fibres in (dark grey) PP. Grey areas between fibres and PP are cracks and voids.

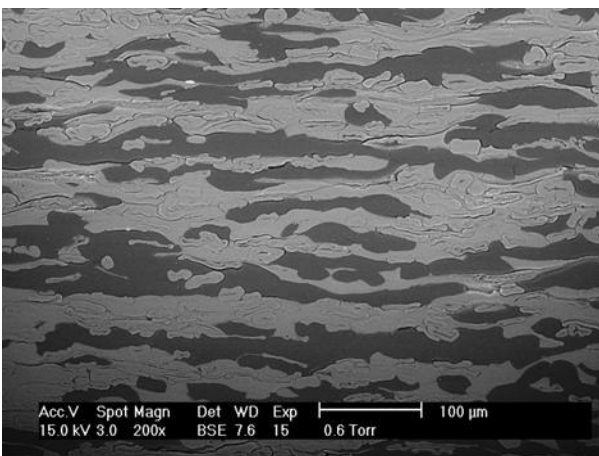


Figure 4e: Micrograph of PLA/PP composite with 40% reference fibres. Fibres are dispersed in PLA (light gray), only few fibres are surrounded by PP (dark grey).

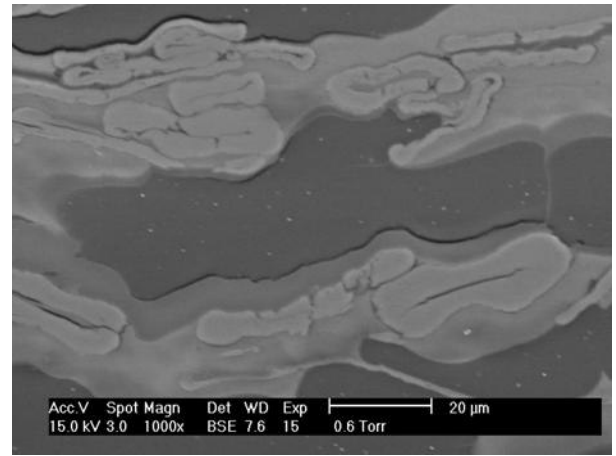


Figure 4f: Micrograph of PLA/PP composite with 40% reference fibres. PLA shows high affinity to wood fibres.



### **3.4 Microscopy**

Poor wetting of the samples leads to cracks and voids in the material. Figs 6a and 6b show micrographs of PLA composites with 60% and 70% reference fibres, respectively. For 70% fibres air pockets are visible in the material (darker gray). For 60% fibres the dispersion is good, but in-plane cracks are visible. When micrographs of composites with reference fibres or BTCA modified fibres are compared a difference in fibre dispersion is seen. The BTCA treated fibres show fibre aggregates and areas where fibres are sparse. The reference fibres show fibre couplings in a more even fibre distribution. Composites with PP and 40% reference and BTCA treated fibres are shown in Figs 6c and 6d, respectively. The poor properties of composites with PP and BTCA treated fibres is explained by the cracks and voids (grey) surrounding the fibres (light grey), separating them from the PP matrix (dark grey), Fig. 6d. The effect of the hydrophobic nature of PP is seen in Figs 6e and 6f. The micrographs show a composite with mixed PLA-PP matrix. It is clearly seen that the PLA (light grey) shows higher affinity to wood fibre surface compared to PP (dark grey). The micrographs also show that PLA and PP are immiscible. PLA can be regarded as a compatibilizer, forming an interface between the fibres and the PP matrix.

### **4 CONCLUSIONS**

Effects of BTCA modification, choice of matrix and fibre fraction on hygroexpansion and diffusion of wood-fibre composites were investigated. The BTCA modification proved to reduce the water retention and moisture sorption of the fibres and showed reduced out-of-plane swelling and diffusion for composites where PLA was used as matrix material. For BTCA-PLA composites with high fibre content the hygroexpansion was one third of composites with where reference fibres were used. Micrographs showed that PLA and fibres commingled well and only a few percent of the swelling remained after redrying. The combination of BTCA modified fibres and PP matrix was not successful. Together with PP the BTCA modified fibres increased the swelling of the composites. The quality of these composites was low with aggregated fibres and cracks between fibres and matrix and only a few percent of the swelling of these composites were reversible, hence the samples were permanently damaged. This suggests that the weak fibre-matrix interface was destroyed during swelling or by the moisture. Composites with a mixture of PLA and PP as matrix material showed the same trends as composites where pure PLA was used, with reduced swelling when BTCA modified fibres were used. Micrographs showed that the fibres were surrounded by PLA and had less contact with PP. The fibre fraction was however the most important parameter to the out-of-plane hygroexpansion of all materials, high fibre fraction leading to high hygroexpansion.

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