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ORIGINAL

The effect of chemical treatments of natural fibres on the properties of phosphate-bonded composite products

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Abstract Phosphate-bonded composites are an emerging class of building materials produced from natural fibres and phosphate based cement pastes. They are durable and possess mechanical properties similar to those of Portland cement. However, the moisture absorption of natural fibre can lead to swelling which may result in the reduction in the mechanical strength properties and eventually negatively affect the long-term performance and dimensional stability of the products. This study was aimed at the modification of some properties of selected biomaterial residues in order to enhance the final properties of the phosphate-bonded composite product. Three different treatments were evaluated viz. 1% caustic alkali, 1% acetic anhydride and hot water on natural fibres derived from slash pine, black wattle and bagasse. The effect of the treatment on the fibres was evaluated via HPLC, SEM and FTIR. Further, the performance of the treated fibres was evaluated in composite panels bonded with magnesium phosphate ($MgPO_4$) and calcium phosphate ($CaPO_4$) cement pastes against the controls. The manufactured panels were tested for flexural properties and dimensional stability. In the $MgPO_4$-bonded panels, the MOR increased from 0.55 MPa for untreated bagasse panels to 0.79 MPa for alkalised panels. Similarly, the MOE increased from 150.04 MPa for untreated bagasse panels to 175.65 MPa for alkalised panels. In untreated $MgPO_4$-bonded panels, the mean density was 0.76, 078 and 0.75 g/cm^3, while in alkalised panels, the mean density was 0.81, 0.81 and 0.81 g/cm^3 for wattle, pine and bagasse panels, respectively. In the bagasse panels, the water absorption was 54.61% for untreated, 48.74% for hot water extracted, 42.21% for acetylated and 36.44% for alkalised $MgPO_4$-bonded panels. This represents a percentage improvement of 11, 23 and 33%, respectively. Alkali-treated fibres had the best effect overall for all measured properties.

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Introduction

Lignocellulosic natural fibres have the potential to be used as replacements for traditional reinforcement materials in composites because of their stiffness, impact resistance and flexibility (Sgriccia et al. 2008). In addition, natural fibres are renewable and biodegradable, and possess several other desirable properties such as high tensile strength and modulus of elasticity, which are currently being exploited in many fields of composite technologies including biocomposites and nanocomposites. The wide-spread availability and low cost are some of the factors responsible for the renewed interest and research on natural fibres for use in composite manufacturing. Apart from the availability of valuable raw materials for biocomposite production, the industrial exploitation of these materials contributes to the protection of the environment (absorption of CO_2) and gives economic potential to developing countries (Papadopoulou et al. 2015).

The manufacturing of chemically bonded phosphate composite products relies on the reaction between an alkali metal oxide and a weak acidic phosphate to form a sparingly soluble salt (Wagh 2004). This reaction is highly exothermic and sets into a solid mass within minutes with a high initial strength. However, the behaviour and strength development of the composites is likely to be affected with the addition of natural fibres. As with concrete and other cementitious composites, the major limitations to the use of natural fibres in chemically bonded composites include the sensitivity to moisture and variable fibre properties, coupled with the inherent incompatibility between the hydrophilic fibres and the hydrophobic matrix. The hydrophilicity of natural fibres results in high moisture absorption and weak adhesion with hydrophobic matrices. These limitations result in inadequate fibre distribution in the matrix and subsequently poor stress transfer from the matrix to the fibres (Hajiha et al. 2014). Hence, the ultimate strength of phosphate-bonded natural fibre composites is a fraction of the strength of the pure matrix. Similarly, the mechanical properties of biocomposites depend largely on the interfacial bonding between the fibres and the matrix.

Natural fibres can be modified to reduce the amount of hydrophilic hydroxyl groups and improve the adhesion to matrix materials (Kabir et al. 2011; Hajiha et al. 2014). There are different physical and chemical treatment methods that have been employed to modify the surfaces of natural fibres. Surface fibrillation, cold plasma treatment and electric discharge method, for example, are physical treatments that can alter the surface properties of fibres and enhance mechanical bonding between fibres and matrix (Mohanty et al. 2005; Abdelmouleh et al. 2007). Chemical treatment of fibres is widely used to reduce the hydrophilic properties of natural fibres and improve compatibility with the matrix. Several chemical treatments including alkalisation, acetylation, salinisation, benzoylation and peroxidation have been applied to modify the surfaces of natural fibres and improve their properties.

Amiandamhen et al. (2016) proposed the optimisation of the manufacturing conditions for phosphate-bonded composite products using response surface methodology optimisation. While the physical properties of the boards produced met the minimum requirements for cement-bonded particleboards according to EN 634-2 (2007), some properties such as the bending strength could still be improved to offer more flexibility in terms of application of the products. The current study employed three fibre surface treatments, viz. caustic alkali, acetic anhydride and hot water treatments in an attempt to improve the properties of the composite products. These treatments were selected based on affordability and results from previous studies that investigated the effect of surface treatments on the properties of natural fibres. In general, alkaline treatment changes the orientation of crystalline cellulose and forms amorphous regions by swelling the fibre cell wall. It also reduces the lignin and hemicelluloses content, as well as volatile products through the rupture of alkali sensitive hydrogen bonds (Li et al. 2007). This combined effect partially removes the hydrophilic hydroxyl group (Eq. 1) and improves moisture resistance (Kabir et al. 2011).

$$\mathrm{Fibre-OH+NaOH\rightarrow Fibre-O-Na+H_2O} \tag{1}$$

In addition, the stress transfer capacity between fibre cells is improved due to the improved fibre-matrix interfacial adhesion. Acetylation, which is generally known as an esterification method, is used to stabilise the cell walls against moisture absorption by plasticising the cellulose fibres. Fibres may be acetylated with or without an acid catalyst to graft acetyl group onto the cellulose structure (Kabir et al. 2011). The acetyl group replaces the hydroxyl group (Eq. 2) resulting in improved dimensional stability of the composites. Esterification also causes cellulosic fibres to be more compatible with hydrophobic matrices.

$$\mathrm{Fibre-OH+CH_3-C\,(=O)-O-C\,(=O)-CH_3\rightarrow Fibre-O-C\,(=O)-CH_3+CH_3C\,(=O)-OH} \tag{2}$$

Hot water hydrolysis remains the oldest and cheapest method of fibre treatment. Hot water extraction is an autocatalytic thermochemical process for the fractionation of easily accessible sugars in natural fibres (Pelaez-Samaniego et al. 2014). Hot water hydrolysis depolymerises hemicellulose into monomers and oligomers with partial depolymerisation of cellulose and lignin (Garrote et al. 1999). Lignin may also be subjected to partial solubilisation and plasticisation (Pelaez-Samaniego et al. 2013). These reactions alter the chemical composition and properties of the fibres. Thus, the treated fibres have improved properties for composite manufacturing in terms of lower water affinity and better dimensional stability (Boonstra et al. 2006).

It is proposed that these treatments would improve the fibre surface morphology, which may enhance the bonding of the fibres with the phosphate matrix. Therefore, this study investigated the effect of the selected fibre surface treatments on the physical and flexural properties of phosphate-bonded composite products. The flexural properties were evaluated as the composites would be applied in load-bearing applications and are not expected to be subjected to sudden impact or tensile loadings.

Experimental

Materials

Dried industrial crushed sugarcane bagasse (*Saccharum officinarum*) supplied by TSB Sugar Ltd., South Africa, black wattle (*Acacia mearnsii*) supplied by EC Biomass Fuel Pellets (Pty) Ltd., Port Elizabeth, and slash pine (*Pinus elliottii*) supplied by Cape Pine, a local subsidiary of the Global Environment Facility (GEF), were used as the fibre raw materials in this study. Analytical grade NaOH (98% purity), acetic anhydride (98% purity), acetic acid (99% purity) and sulphuric acid (98% purity) were used in the treatment of the fibres. The composite binding matrix was prepared from monopotassium phosphate (MKP 0-52-34), a white crystalline product with > 98% assay. This product was purchased from Shijiazhuang Lvhe Fertilizer Technologies Co. Ltd., China. The study also utilised MAGOXBPPO, a heavy magnesium oxide with 96% minimum assay, purchased from Macco Organiques, Zahradnl, Czech Republic. The unslaked lime was purchased from Bontebok Lime Works (Pty) Ltd., Bredasdorp, South Africa, and it has a minimum assay of 70–88% Ca as CaO. The calcium silicate used was Microcal ET purchased from PQ Corporation, Warrington, UK. It has an assay of > 87% SiO_2 basis and 12–22% CaO.

Fibre treatments

The fibres were treated with hot water and solutions of NaOH and acetic anhydride using a solid/liquid ratio of 1/10 (g/mL). All the treatments were carried out in a 5-L stainless steel laboratory size pulp digester, and the pre-determined temperature settings were controlled by a proportional integral derivative (PID) system (Beckermann and Pickering 2008). Fibres treated with hot water were heated to a temperature of 100 °C for 1 h as described by Ferraz et al. (2016). Alkalisation was carried out at 60 °C for 1 h according to a method described by Oladele et al. (2015). According to this method, a 0.25 M NaOH solution (1 wt%) was prepared to treat the fibres. The treatment was meant to be less severe than actual de-lignification in alkaline pulping process. Fibres treated with acetic anhydride were heated to a maximum temperature of 90 °C for 1 h as described by Bledzki et al. (2008). Acetylation was carried out using a 1 wt% solution of acetic anhydride with 0.1 wt% sulphuric acid as buffer. The ester was prepared from a 1:1.5 ratio of acetic anhydride to acetic acid (Hajiha et al. 2014). After each treatment, the fibres were washed with distilled water until neutral pH was reached. Thereafter the treated fibres were dewatered using a spin dryer. The wet fibres were oven-dried at 60 °C for 24 h and then conditioned at 20 °C and 65% relative humidity (RH) for 72 h. Subsequently, the fibres were weighed to determine the fibre yield from each treatment.

Chemical analyses of the fibres after treatment

The aim of the study was to modify the fibres to improve the eventual properties of the board products. The effect of treatment on the chemical composition and yield of the fibres was determined through chemical analysis of treated fibres in comparison to the controls. The ash content was determined according to TAPPI T211 (2004) by heating 2.0 g of oven-dried material at 525 °C for 3 h after which the residue was weighed. The acid-insoluble lignin was determined according to the National Renewable Energy Laboratory (NREL) Analytical Procedure (LAP 013) (Sluiter et al. 2012). According to this method, 3 mL of 72% sulphuric acid was added to 0.3 g of material in a test tube, stirred and placed in a water bath at 30 °C for 1 h. The material was washed with 84 mL distilled water into a flask to dilute the acid concentration to 4%. The solution was then heated in an autoclave for 90 min. The sample was transferred quantitatively on a crucible and washed with 250 mL boiling water. Acid-insoluble lignin was determined as the mass of residue after drying at 105 °C and based on the oven dry sample. The sugar composition, i.e. glucose, cellobiose, xylose and arabinose was determined from the hydrolysate via high pressure liquid chromatography (HPLC). The HPLC system used for quantification was comprised of a spectra system P2000 pump, an auto-sampler (AS3000), a UV1000 detector and a Shodex RI-101 refractive index detector. The sugars were measured with the RI detector and the column was operated at 65 °C with a mobile phase of 5 mM H_2SO_4 and a flow rate of 0.6 mL min^{-1} (Vena et al. 2010).

Fourier transform infrared spectrophotometer (FTIR)

FTIR was performed to identify chemical changes in functional groups of the untreated and treated fibres. FTIR was conducted with a Thermo-Scientific Nicolet iS10 model consisting of an attenuated total reflectance unit and a transmission-FTIR unit. A minimum of 32 scans were run in the range of 500–4000 cm^{-1} and a resolution of 4 cm^{-1}.

Scanning electron microscopy (SEM)

SEM analysis of the fibres was performed to study the effect of the treatments on the morphological characteristics of the fibres at a magnification of 1.0 K X. The samples were mounted on metal stubs with double-coated carbon adhesive tape. The samples were thereafter sprayed with carbon using a high vacuum S150A sputter coater prior to the imaging. The micrographs of the treated and untreated fibres were examined using a LEO 1430VP MERLIN FE-SEM equipped with an energy dispersive X-ray spectrometer (EDS) GENESIS XM2. EDS was performed using a focussed beam of X-rays at random positions into the samples at a magnification of 500×.

Composite fabrication

Two types of phosphate binders were fabricated in the study using pre-treated materials against the controls. They include magnesium phosphate ($MgPO_4$) and calcium phosphate ($CaPO_4$). Magnesium phosphate-bonded composite boards were prepared according to an optimised method proposed by Amiandamhen et al. (2016). According to this method, the fibres were milled using a hammermill fitted with a 1 mm sieve. The dimension of the fibres was not considered in this study. However, the fibres used were less than 1 mm long. The screened fibres were conditioned at 65% RH and 20 °C for 72 h. Thereafter, the materials were measured and mixed thoroughly with a magnesium phosphate on a binder/fibre ratio as described by Amiandamhen et al. (2016). Calcium phosphate based boards were prepared according to a method proposed by Amiandamhen et al. (2017). According to this method, the optimum binder ratio of monopotassium phosphate to unslaked lime and calcium silicate was 8.73:1, while the binder/fibre ratio was 3.34:1 for black wattle and pine, and 11:1 and 3.26:1 for bagasse, respectively. For both board types, a pre-determined amount of water was added to the mix as pre-calculated by Amiandamhen et al. (2016). The materials were mixed until homogeneity was achieved. The mixture was poured into a metallic mould measuring $218 \times 77 \times 40$ mm^3 and cold-pressed at 200 kPa for 5 min. The final thickness of the formed panel was 13 mm due to a 27-mm thick steel bar placed in the mould. The panel was de-moulded and weighed to calculate its wet specific gravity. The panels were stacked in ambient temperature to dry over a period of 14 days, after which they were weighed at intervals to determine the loss in panel weight. The untreated and treated fibres were used in the fabrication of the composite panels. After drying, the panels were conditioned at 65% RH and 20 °C for 72 h prior to testing.

Composite testing

The properties of the formed panels were evaluated to investigate the effect of fibre treatment on the flexural strength and dimensional stability of the composites. Flexural test specimens were tested according to ASTM D1037-13 using an Instron testing machine fitted with a 5 kN load cell, operated at a rate of 5 mm/min. The specimens were tested to failure and the modulus of rupture (MOR) and apparent modulus of elasticity (MOE) were calculated from the formula outlined in ASTM (2013). Water absorption (WA) characteristics and thickness swelling (TS) tests were carried out by submerging conditioned specimens horizontally in fresh water for 24 h. After submersion, the specimens were suspended to drain for 10 min and excess water was removed from the surface. The specimens were weighed and the thickness was determined as an average of four measurements. The WA of the specimen was calculated from the increase in weight and expressed as a percentage of the conditioned weight, while the TS of the specimen was calculated as a percentage of the conditioned thickness.

Micro computed tomography (µCT)

Based on the outcome of the composite tests, µCT was used to characterise and compare the microstructure of the pre-treated fibre-based composites against the controls. For this purpose, only the boards prepared from alkali-treated fibres were evaluated due to their overall better performance as well as cost of the technique. A numerical technique was used to quantify the cement matrix, fibre and void phases and their distribution in the samples. The composite samples were cut with a band saw into nominal dimensions of $10\times10\times13$ mm^3. The samples were placed on the rotation stage and probed with a polychromatic X-ray beam using a General Electric Phoenix VTomeX L240 microCT scanner equipped with the Datos reconstruction software. The Volume Graphics VGStudio Max3 was used to construct 3-D images of the composites from stacks of 2-D images. The 3-D images were used to generate the actual phase distribution for void, fibre and cement matrix within the specimens. Two-phase segmentation steps were performed, i.e. between the matrix, fibre and voids, and between the voids, matrix and fibre. These two segmentations were combined to delineate the fibre phase. Data sets were visualised in 2- and 3-D using volume rendering in which a transfer function assigns each voxel a colour and transparency (Evans et al. 2010). Volume rendering was performed using the VGStudio Max3. Numerical values were derived for the volumes of fibre, matrix and void across the thickness of a representative board sample using maximal sphere modelling. Thereby, for every point within the board, the diameter of the largest sphere is defined which fully lies within the void, matrix or fibre phase and covers that point (Evans et al. 2010).

Experimental design and data analysis

The experiment was laid out in a completely randomised design with four replications. The data were analysed using STATISTICA (V13) to evaluate the effects of fibre treatments on the physical and mechanical properties of the panels. Duncan's multi-stage range test was used in the separation of means for comparison.

Results and discussion

Effect of the treatment on fibre yield and characteristics

Yield and chemical composition

Generally, mild conditions including low chemical concentrations, low temperature and short contact duration were employed so that the fibres were not significantly degraded. The bagasse fibre yields were 97.1, 87.9 and 92.1% for hot water treatment, alkali treatment and acetic anhydride treatment, respectively. The pine fibre yields were 93.7, 90.3 and 96.5% for hot water treatment, alkali treatment and acetic

Table 1 Yield and chemical composition of untreated and treated fibres (%)

Fibres	Treatment	Lignin	Glucose	Xylose	Ash	Yield
Wattle	Untreated	18.17 ± 1.0	42.73 ± 5.0	10.81 ± 1.31	0.47 ± 0.001	
	Hot water	17.42 ± 3.63	40.14 ± 0.48	10.09 ± 0.15	0.47 ± 0.001	91.7
	Acetylation	17.71 ± 2.50	41.84 ± 1.17	9.96 ± 0.53	0.10 ± 0.000	92.1
	Alkalisation	16.07 ± 4.32	42.95 ± 0.40	9.79 ± 0.23	1.94 ± 0.002	87.2
Pine	Untreated	27.32 ± 1.40	36.29 ± 0.92	12.07 ± 0.29	0.40 ± 0.001	
	Hot water	26.31 ± 1.25	38.36 ± 2.46	12.47 ± 0.87	0.37 ± 0.000	93.7
	Acetylation	25.02 ± 0.97	41.54 ± 0.05	13.75 ± 0.30	0.16 ± 0.000	96.5
	Alkalisation	25.27 ± 0.94	44.08 ± 1.08	14.07 ± 0.49	2.51 ± 0.01	90.3
Bagasse	Untreated	23.33 ± 4.17	40.20 ± 0.79	11.40 ± 0.29	2.55 ± 0.003	
	Hot water	23.56 ± 3.32	39.07 ± 1.66	10.62 ± 0.29	2.16 ± 0.001	97.1
	Acetylation	21.66 ± 0.93	37.41 ± 2.44	10.45 ± 0.58	2.40 ± 0.001	92.1
	Alkalisation	13.47 ± 2.72	48.68 ± 4.22	15.00 ± 2.85	3.14 ± 0.001	87.9

Values represent mean of three replicates and SD

anhydride treatment, respectively. The wattle fibre yields were 91.7, 87.2 and 92.1% for hot water treatment, alkali treatment and acetic anhydride treatment, respectively. The yield from alkalisation was the lowest for all three species, probably due to partial removal of some fibre components in the black liquor (Table 1). As the treatments were not meant to be destructive on the raw material, high values were obtained compared to such processes as conventional Kraft or soda pulping which are about 45–65% (Kanungo et al. 2009; Vena et al. 2010).

In general, the presence of soluble sugars in natural fibres inhibits the hydration of Portland cement-bonded composites (Karade et al. 2003), making pre-treatment of fibres an option which can be costly. Phosphate binders, on the other hand, are not known to be affected by the sugars and hemicelluloses in natural fibres. However, the presence of hydroxyl groups in sugars and other carbohydrates may affect the durability of the composites. This study was carried out to determine the effect of pre-treatments on the chemical properties of the fibres and the composite properties. The chemical composition of the untreated and treated fibres is presented in Table 1. All the treatments reduced the lignin content in the fibres, but the effect was less in hot water treated fibres. Hot water hydrolysis depolymerises hemicelluloses into monomers and oligomers with partial depolymerisation of cellulose and lignin (Garrote et al. 1999). Hot water extraction also reduced the total xylose and glucose in wattle fibres. This condition was observed in the FTIR analysis of hot water treated fibres. Alkalisation was observed to proportionally increase the ash content of the fibres. This may be due to the removal of organic matter, which proportionally increases the percentage of the inorganic materials. On the contrary, acetylation decreased the ash content of the fibres. Alkalisation also proportionally increased the xylose and glucose contents in pine and bagasse fibres due to the removal of lignin. Alkalisation had the greatest effect on the lignin content of bagasse fibres. The HPLC analysis did not detect any traces of arabinose and cellobiose in the fibres.

SEM analysis

In general, the treatments resulted in defibrillation of the fibres which may increase mechanical interlocking with the cement matrix. Acetylated and alkalised fibres showed cleaner surfaces due to the removal of waxy substances and lignin from the fibre surface during treatments. Cleaner surfaces were not obtained for the treated pine fibres. It is expected that the cleaner surfaces result in better bonding with coupling agent during composite development (Li et al. 2007; Pickering et al. 2007; Hajiha et al. 2014). The SEM micrographs show the surface morphologies of treated and untreated fibres for the three species (Figs. 1, 2, 3; magnification = 1 K X; scale bar = 10 μm). Differences were observed in the alkali-treated fibres where surface impurities such as waxes and pectin were removed. This was also observed in other studies (Pickering et al. 2007; Le Troedec et al. 2008; Hajiha et al. 2014). Acetylation was also found to remove some impurities from the fibre surfaces as observed in the wattle and pine fibres. It is believed that waxy substances of the fibres are removed (Tserki et al. 2005) and hydroxyl groups are replaced by acetyl groups (Li et al. 2007; Hajiha et al. 2014), making the fibres less hydrophilic. There were no differences in the SEM micrographs of untreated and hot water-extracted fibres of pine and bagasse. Hot water-extracted fibres show evidence of impurities on the surface of the fibres indicating that the treatment was not efficient in cleaning the fibres. It is however, believed that hot water extraction alters the chemical composition of

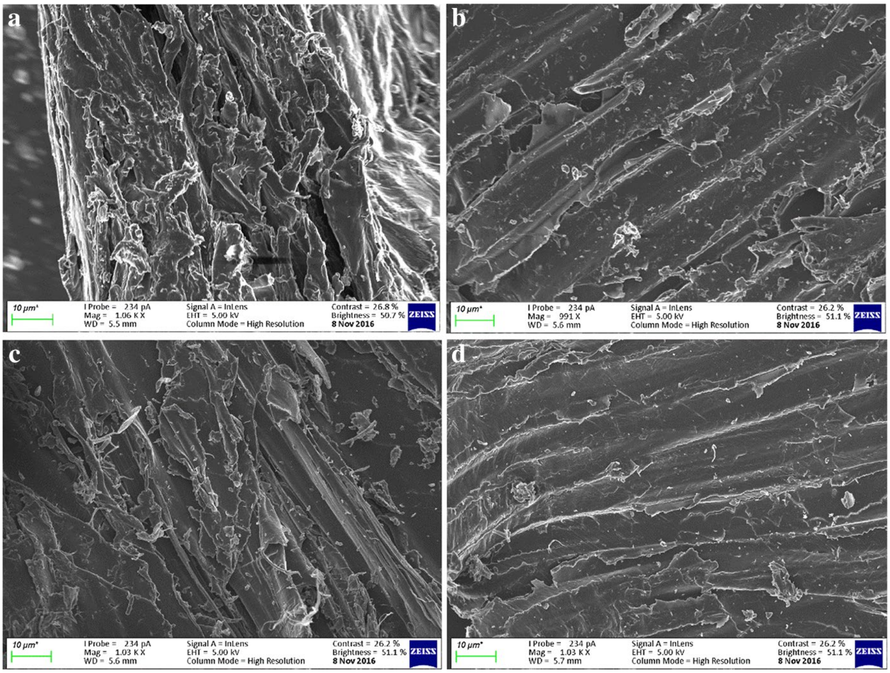

Fig. 1 SEM micrograph of **a** untreated wattle fibres, **b** hot water-extracted wattle fibres, **c** acetylated wattle fibres, **d** alkalised wattle fibres

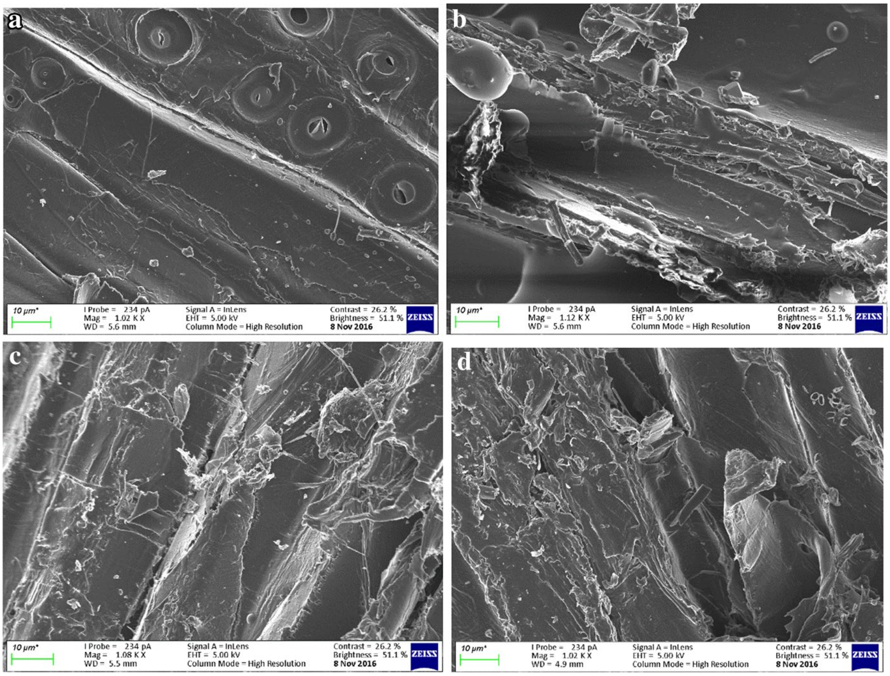

Fig. 2 SEM micrograph of **a** untreated pine fibres, **b** hot water-extracted pine fibres, **c** acetylated pine fibres, **d** alkalised pine fibres

fibres by fractionating easily accessible sugars and hemicelluloses (Pelaez-Samaniego et al. 2013, 2014).

Energy dispersive spectroscopy (EDS) was used to characterise the treated and untreated fibre samples. The spectral diagrams obtained were used to generate the elemental composition of the samples and the means of two random observations are presented in Tables 2, 3 and 4 for each species. It was observed that all fibres contain carbon, oxygen, sodium, potassium and calcium, while magnesium, aluminium, silicon, iron and copper were only detected in some samples. The treatments were observed to be effective in removing sodium from the fibres. Untreated bagasse fibres were more hydrophobic than untreated wattle and pine fibres due to the higher C/O ratio. According to Sgriccia et al. (2008), cellulose, hemicellulose and pectin have a C/O ratio of 1.21, while lignin has a ratio of 2.86. Since the treated and untreated samples have C/O ratios greater than 1.21, this shows that some wax and lignin remained in the fibres. It is important to note that actual C/O ratios of the samples may be lower than the obtained values. This is due to the additional amount of carbon used in coating the samples prior to SEM.

FTIR spectroscopy

The FTIR spectra of the untreated and treated fibres are shown in Figs. 4, 5 and 6. The C–H symmetric stretch around 2916 cm^{-1} is present in all fibres

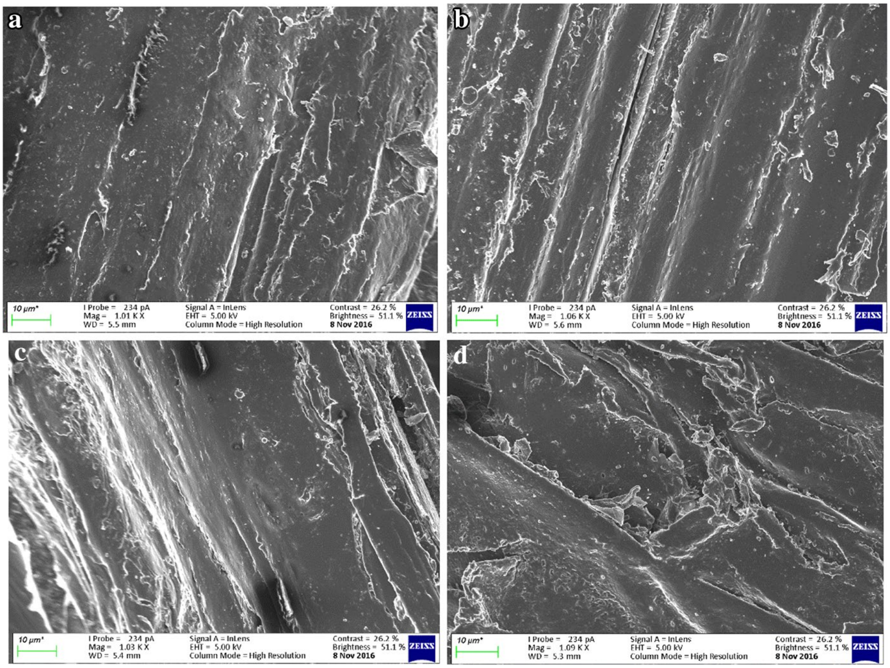

Fig. 3 SEM micrograph of **a** untreated bagasse fibres, **b** hot water-extracted bagasse fibres, **c** acetylated bagasse fibres, **d** alkalised bagasse fibres

Table 2 Elemental composition (%) of surface treated wattle fibres

Spectral label	Untreated	Hot water	Acetylated	Alkalised
C	55.7	58.18	60.91	59.31
O	42.2	41.76	38.73	40.46
Na	0.9	–	–	–
Si	–	0.08	–	–
Cl	–	–	0.09	–
K	0.07	0.05	0.21	–
Ca	0.18	–	0.09	0.14
Cu	–	–	–	0.22
C/O ratio	1.32	1.39	1.57	1.47

C-content values are slightly higher than the actual values. All fibres were coated with a thin layer of carbon prior to microscopy

except alkalised pine fibres. The intensity of the peak was highest in hot water extracted bagasse (Fig. 4). The peak at 3303 cm^{-1} is also present in all fibres examined. This peak corresponds to the axial stretching of hydroxyl group (–OH) (Sawpan et al. 2011). The CH_2 peaks at around 1415 cm^{-1} are present in all treated and untreated fibres. This peak signifies the existence of the symmetric bending of cellulose (Hajiha et al. 2014), while the peak at 1223 cm^{-1}

Table 3 Elemental composition (%) of surface treated pine fibres

Spectral label	Untreated	Hot water	Acetylated	Alkalised
C	56.33	60.72	59.64	58.77
O	42.78	39.14	39.95	40.20
Na	0.78	–	0.12	–
Mg	–	–	–	0.22
Si	–	–	–	0.09
P	–	0.09	–	0.18
Cl	–	0.05	0.12	–
K	0.09	0.16	0.21	0.27
Ca	0.06	–	0.1	0.16
Cu	–	–	–	0.13
C/O ratio	1.32	1.55	1.49	1.46

C-content values are slightly higher than the actual values. All fibres were coated with a thin layer of carbon prior to microscopy

Table 4 Elemental composition (%) of surface treated bagasse fibres

Spectral label	Untreated	Hot water	Acetylated	Alkalised
C	58.91	62.19	63.37	62.11
O	38.97	37.21	32	35.23
Na	0.89	–	–	–
Mg	0.13	0.1	0.16	0.12
Al	0.13	0.1	0.09	0.18
Si	0.3	0.2	4.01	1.87
P	0.1	0.08	0.12	0.05
S	0.05	0.08	0.05	0.06
Cl	0.09	0.05	0.09	–
K	0.17	0.11	0.24	–
Ca	0.17	0.09	0.09	0.28
Fe	0.17	–	0.1	0.24
Cu	0.12	–	–	–
C/O ratio	1.51	1.67	1.98	1.76

C-content values are slightly higher than the actual values. All fibres were coated with a thin layer of carbon prior to microscopy

represents the C–O–C asymmetric bridge stretching of lignin (Kaczmar et al. 2011). These peaks are, however, minimal in alkalised pine fibres (Fig. 5), indicating that there was partial removal of the fibre materials (also see Table 1). The C–C stretching was also present at 1023 cm^{-1}, and this relates to the β-glucosidic linkages between the sugar units in hemicelluloses and cellulose (Sawpan et al. 2011; Hajiha et al. 2014). The peak at 1730 cm^{-1} is present in all the acetylated fibres as well as in the hot water-extracted fibres of bagasse and wattle (Figs. 4, 6). It is also present in untreated pine fibres (Fig. 5). This

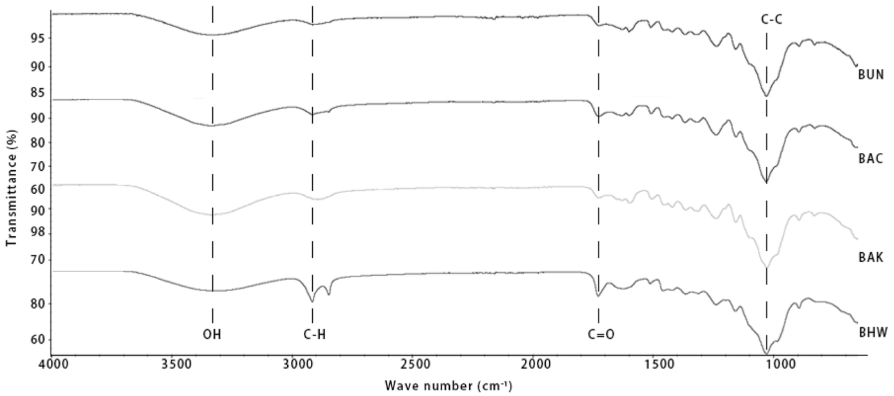

Fig. 4 FTIR spectrum of treated and untreated bagasse fibres (BAK, alkalised; BAC, acetylated; BHW, hot water extracted; BUN, untreated)

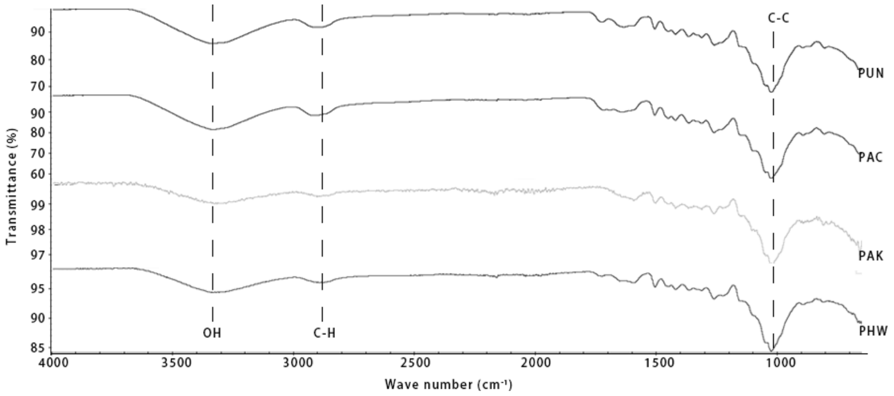

Fig. 5 FTIR spectrum of treated and untreated pine fibres (PAK, alkalised; PAC, acetylated; PHW, hot water extracted; PUN, untreated)

peak is usually attributed to the C=O stretching of the acetyl groups of hemicelluloses (Liu et al. 2004). The intensity of this peak decreases after hot water extraction and alkalisation in pine and wattle (Figs. 5, 6), indicating that hemicelluloses were partially removed. This was also observed by Pelaez-Samaniego et al. (2014). The peak was, however, not affected by acetylation. It is evident in this study that the peak may have been enhanced due to the acetylation treatment, since the peak is not stretched in the untreated fibres of the other species. The intensity of the broad band at 3217–3368 cm^{-1} showed partial removal of the OH group in alkali and hot water treated pine (Fig. 5). There were no important changes after treatment in bagasse and wattle (Figs. 4, 6). Since these bands are assigned to the hydrogen-bonded OH groups in intramolecular

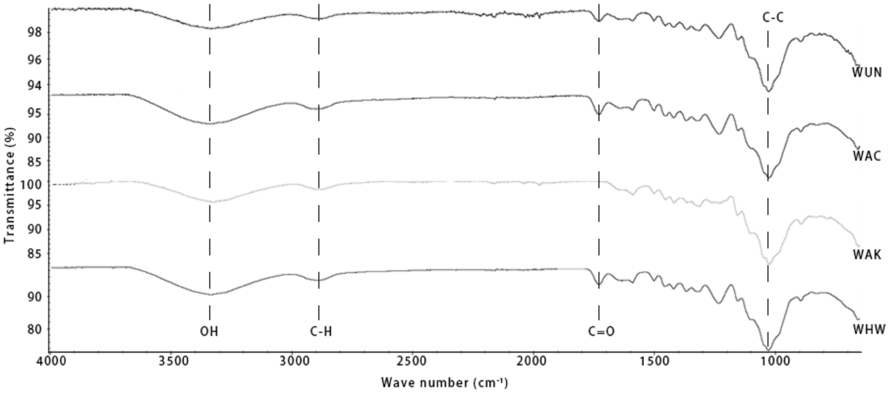

Fig. 6 FTIR spectrum of treated and untreated wattle fibres (WAK, alkalised; WAC, acetylated; WHW, hot water extracted; WUN, untreated)

cellulose (Kobayashi et al. 2009), it appeared cellulose was not degraded in both species during the treatments.

Effect of the treatment on panel properties

Data analysis

The data were analysed using the one-way ANOVA by STATISTICA (V13). The analysis revealed that treatment had a significant effect on MOR, WA and TS of all the panels ($p < 0.05$). The effect of the treatments was significant on the properties of the bagasse panels, except for the density (Table 5). Since density plays a major role in determining the strength properties of composite panels, the treatment also influenced the MOR, but the effect on the MOE was not significant except for bagasse panels. Table 6 shows the comparison of means using Duncan's multi-stage range test. Although the effect of the treatment was not significant on the MOE of pine panels, there was a difference between the means. The same observation was made for density of bagasse panels. However, there was no difference between the means in the MOE of black wattle panels (Table 6).

Table 5 *p* values showing the effect of treatment on the properties of the panels

Property	Black wattle	Slash pine	Bagasse
Density	0.000*	0.000*	0.171
MOR	0.007*	0.048*	0.000*
MOE	0.246	0.273	0.000*
WA	0.026*	0.000*	0.000*
TS	0.002*	0.000*	0.000*

*Denotes values that are significant ($p < 0.05$)

Table 6 Mean comparison using Duncan's multi-stage range test

Panels	Property				
	Density (g/cm^3)	MOR (MPa)	MOE (MPa)	WA (%)	TS (%)
BUN1	0.75^{ab}	0.55^{b}	150.04^{ac}	54.61^{a}	4.91^{c}
BHW1	0.76^{ab}	0.73^{a}	156.08^{abc}	48.74^{de}	4.32^{bc}
BAC1	0.79^{ab}	0.80^{a}	165.42^{b}	42.21^{c}	3.61^{ab}
BAK1	0.81^{ab}	0.79^{a}	175.65^{ab}	36.44^{b}	3.35^{a}
BUN2	0.70^{a}	0.43^{c}	134.73^{d}	55.25^{a}	8.15^{d}
BHW2	0.74^{ab}	0.55^{b}	144.61^{cd}	51.82^{a}	7.91^{d}
BAC2	0.78^{ab}	0.75^{a}	157.83^{ab}	43.74^{cd}	5.97^{e}
BAK2	0.85^{b}	0.80^{a}	159.75^{ab}	33.24^{b}	4.21^{abc}
PUN1	0.78^{ab}	0.69^{a}	158.20^{a}	45.24^{b}	3.96^{ab}
PHW1	0.78^{a}	0.80^{ab}	197.44^{ab}	44.87^{b}	5.12^{b}
PAC1	0.83^{bc}	0.84^{ab}	202.87^{ab}	34.83^{a}	3.25^{a}
PAK1	0.81^{ab}	1.06^{b}	224.98^{ab}	33.98^{a}	1.73^{c}
PUN2	0.69^{d}	0.62^{a}	245.05^{ab}	44.27^{b}	5.10^{b}
PHW2	0.79^{ab}	0.69^{a}	253.64^{ab}	33.61^{a}	3.64^{a}
PAC2	0.87^{c}	0.77^{a}	270.49^{ab}	27.97^{d}	3.40^{a}
PAK2	0.92^{c}	0.77^{a}	425.44^{b}	23.86^{c}	1.71^{c}
WUN1	0.76^{d}	0.74^{a}	130.68^{a}	34.91^{a}	2.34^{ab}
WHW1	0.80^{b}	1.03^{a}	220.88^{a}	32.24^{ab}	1.29^{a}
WAC1	0.78^{c}	1.20^{ab}	294.12^{a}	30.73^{b}	1.60^{a}
WAK1	0.81^{b}	1.66^{b}	248.28^{a}	30.29^{b}	1.12^{a}
WUN2	0.60^{a}	0.88^{a}	213.11^{a}	35.91^{a}	5.28^{c}
WHW2	0.60^{a}	0.83^{a}	585.98^{a}	35.10^{a}	4.84^{c}
WAC2	0.60^{a}	0.73^{a}	514.42^{a}	33.42^{ab}	4.40^{bc}
WAK2	0.64^{a}	1.18^{ab}	208.99^{a}	32.63^{ab}	2.42^{ab}

Means in the same column with the same or similar letters are not significantly different ($p < 0.05$)

B, bagasse; P, pine; W, wattle; UN, untreated; HW, hot water; AC, acetylated; AK, alkalised; 1, $MgPO_4$; 2, $CaPO_4$

Density

The density of the boards is presented in Table 6. It was observed that the density increased slightly with each treatment compared to untreated panels for wattle, pine and bagasse. A similar pattern was observed for both phosphate-bonded panels. However, the density did not vary in black wattle panels bonded with calcium phosphate, except for alkali-treated panels. Further, treatment did not increase the density of hot water treated pine panels bonded with magnesium phosphate. The increase in density may be due to better interlocking between the fibres and the cement matrix, thereby forming less-porous and solid materials. This behaviour was verified in the µCT numerical analysis, and the effect of this relationship can be observed in the flexural performance of the composites (Figs. 7, 8, 9). Since density is a major

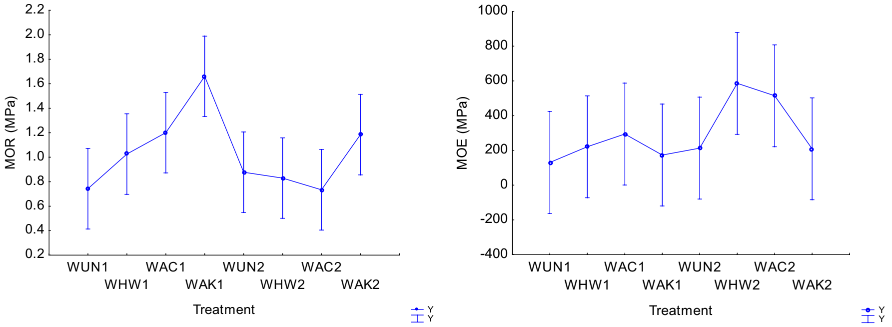

Fig. 7 Trend in MOR and MOE of phosphate-bonded composite panels from black wattle (UN, untreated; HW, hot water; AC, acetylated; AK, alkalised; 1, $MgPO_4$; 2, $CaPO_4$)

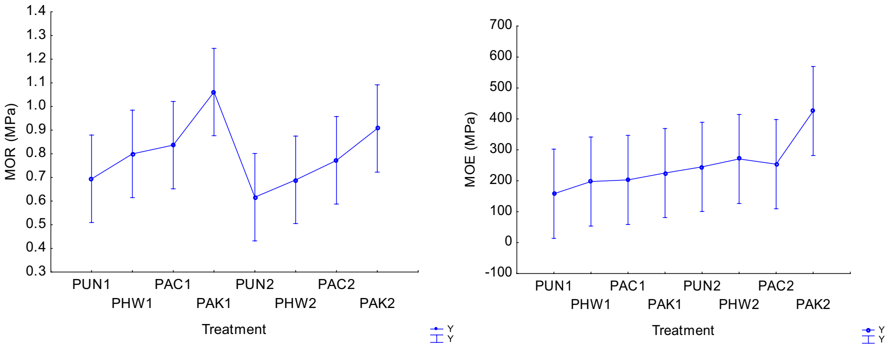

Fig. 8 Trend in MOR and MOE of phosphate-bonded composite panels from slash pine (UN, untreated; HW, hot water; AC, acetylated; AK, alkalised; 1, $MgPO_4$; 2, $CaPO_4$)

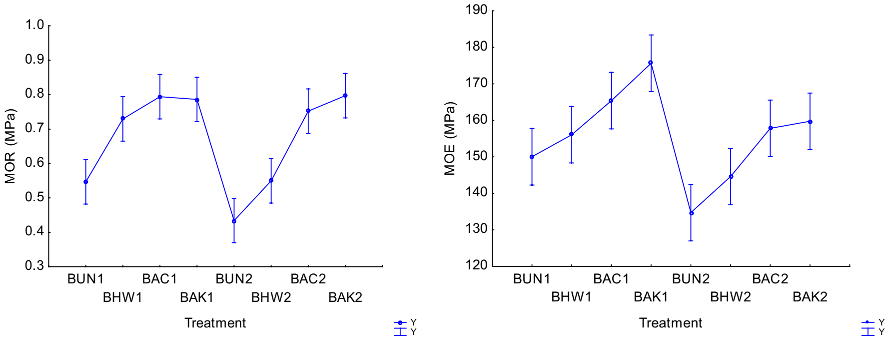

Fig. 9 Trend in MOR and MOE of phosphate-bonded composite panels from bagasse (UN, untreated; HW, hot water; AC, acetylated; AK, alkalised; 1, $MgPO_4$; 2, $CaPO_4$)

determinant of mechanical properties, it is expected that the treatment would also influence the properties of the composite panels.

Flexural properties

The flexural properties of the panels are presented in Figs. 7, 8 and 9. The error bars were drawn to show the variability of the data. Although the variabilities in Figs. 7 and 8 are too high for data comparison, the figures show the trend in the properties as a result of the treatments. In $MgPO_4$-bonded panels of black wattle and pine, the mean MOR increased gradually from untreated to alkalised panels, while $CaPO_4$-bonded panels showed a linear increase in MOR. In $CaPO_4$-bonded panels, both hot water and acetylation caused a decline in the MOR of the composites, but the MOR increased in alkaline treated panels. The increase in MOR in the alkalised panels using both binders could probably be due to the surface modification of the fibres which may have enhanced the bonding with the matrix. A similar pattern of variation was observed in the MOE of the panels. However, treatment did not have a significant effect on the MOE of wattle and pine panels (Table 5). The MOE decreased in alkalised panels compared to acetylated panels for bagasse and wattle (Table 6). The MOE of the panels did not change much for the two binder types, but the alkali-treated $CaPO_4$ pine panels had the highest MOE of 425 MPa. The bagasse treated boards showed a slightly different pattern from the other two species. There was a gradual increase in the MOR and MOE of the panels compared to the untreated panels. Alkalisation resulted in a slight decrease in MOR of the magnesium phosphate-bonded panels. This may be due to the partial degradation of some cellulosic components (as evident in Table 1 and Figs. 4, 5 and 6) during the treatment and the eventual loss in strength of the fibres prior to composite manufacturing.

Dimensional stability

The TS and WA of the composite panels are shown in Figs. 10, 11 and 12. In a similar way, the variability of the data in Fig. 10 is too high for data comparison, however the trend due to the treatments is presented. A decreasing trend in TS and WA can be observed in both $MgPO_4$- and $CaPO_4$-bonded panels after treatment. In all panels, alkalised panels had the lowest TS and WA. This proved that alkali treatment is effective in reducing the hydrophilic groups on natural fibre surfaces. It was also observed that $CaPO_4$-bonded composites generally had high values of TS and WA. This could be due to stronger fibre-matrix adhesion in the $MgPO_4$ composites, which generally inhibits moisture migration to the composites. The pattern of variation is however irregular in pine boards. There was an increase in TS for boards treated with hot water compared to the untreated panels. However, alkalised panels had the lowest TS of the panels. This was not the case with $CaPO_4$-bonded panels, where untreated panels had the highest TS. In bagasse panels, the WA and TS of the panels decreased after treatments with a steep slope.

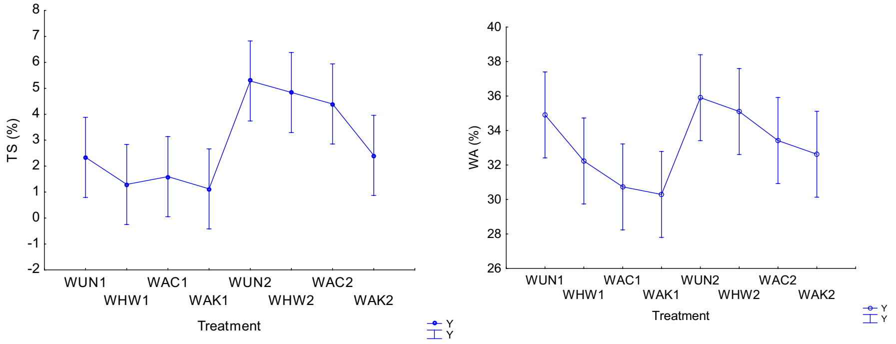

Fig. 10 Trend in TS and WA of phosphate-bonded composite panels from black wattle (UN, untreated; HW, hot water; AC, acetylated; AK, alkalised; 1, $MgPO_4$; 2, $CaPO_4$)

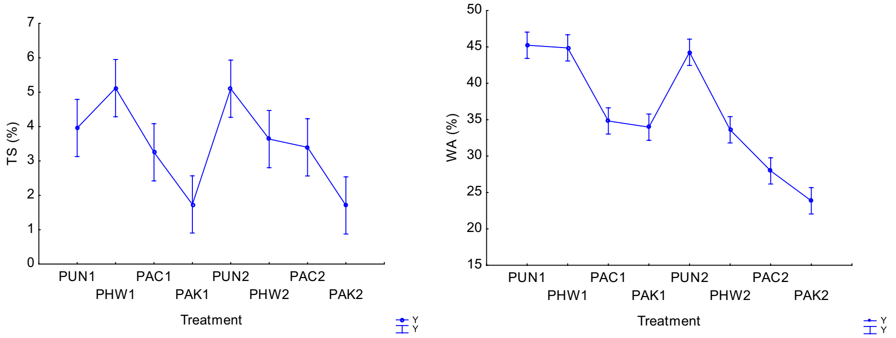

Fig. 11 Trend in TS and WA of phosphate-bonded composite panels from slash pine (UN, untreated; HW, hot water; AC, acetylated; AK, alkalised; 1, $MgPO_4$; 2, $CaPO_4$)

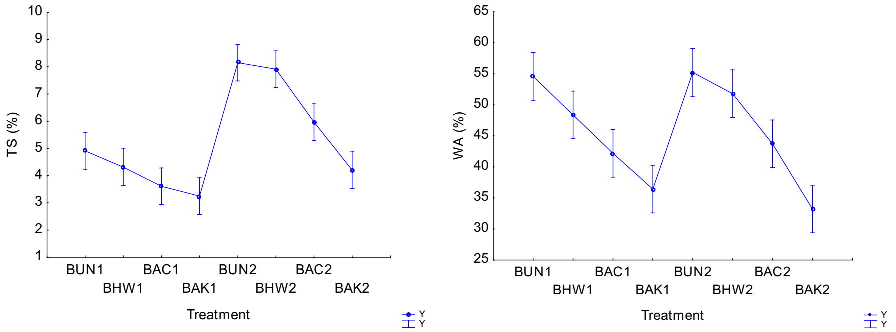

Fig. 12 Trend in TS and WA of phosphate-bonded composite panels from bagasse (UN, untreated; HW, hot water; AC, acetylated; AK, alkalised; 1, $MgPO_4$; 2, $CaPO_4$)

Visualisation of particle distribution in untreated- and alkali-treated composite panels

Distribution of phases in the panels

μCT has been used successfully to examine the structure and interfacial ability of biocomposites materials (Wang et al. 2007; Evans et al. 2010; Kamke et al. 2014; Joffre et al. 2017). In this study, μCT was used to visualise the porous microstructure and distribution of fibres and void phases in the $MgPO_4$-bonded composites produced from untreated- and alkali-treated fibres. The distribution of phases in the panels can be seen in 2-D images selected from tomographic sequences (Figs. 13, 14, 15). In these images, the fibres are grey (A), voids are black (B) and matrix is white (C). Figure 13a, b shows good interparticle contact within the matrix, with few void spaces for untreated- and alkali-treated bagasse composites. Contrarily, Fig. 14a, b shows in-plane views of part of the panel with larger particle sizes and voids. The pine fibres used contained a large proportion of short and thick particles; hence, interparticle contact was poorer. This pattern was also observed by Evans et al. (2010), who reported that the continuity of glue-lines in particleboard appeared to depend on the degree of contact between wood flakes. It was observed that the matrix-lines were longer and more continuous in bagasse (Fig. 13) and wattle (Fig. 15) than in the pine composites (Fig. 14). It was also observed that the matrix distribution was interrupted by the presence of large voids (Figs. 14, 15). However, the adhesive was observed to accumulate in smaller voids creating a ‘spot-welds’ appearance between wood flakes, and around very small particles of ‘fines’ (Evans et al. 2010). The μCT images revealed that the matrix network is continuous in the phosphate-bonded composites. This is similar to the report of Loxton et al. (2003). The authors used confocal laser scanning microscopy (CLSM) to observe UF resin distribution in pressed MDF and wood fibres. They found that the size of

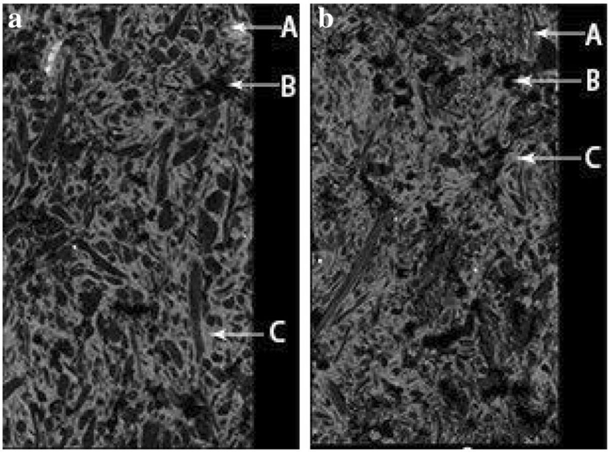

Fig. 13 2-D segmentation of bagasse panel **a** untreated, **b** alkali treated (*A* fibres, *B* voids, *C* matrix)

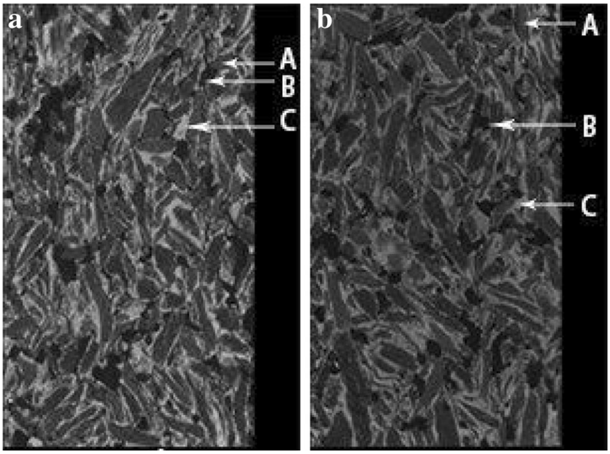

Fig. 14 2-D segmentation of pine panel **a** untreated, **b** alkali treated (*A* fibres, *B* voids, *C* matrix)

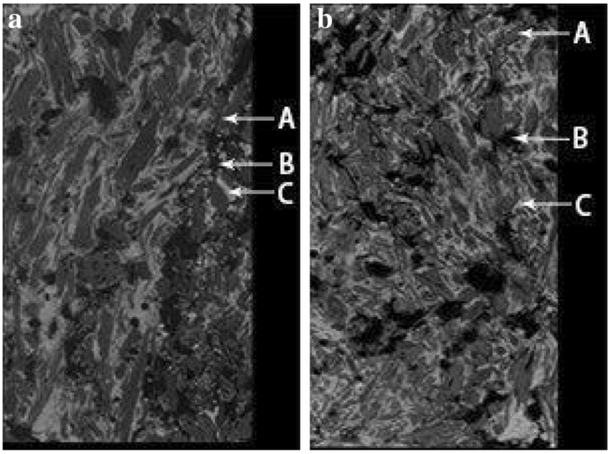

Fig. 15 2-D segmentation of wattle panel **a** untreated, **b** alkali treated (*A* fibres, *B* voids, *C* matrix)

resin spots was greater on fibres in pressed MDF, and this depends on the presence of wax. Evans et al. (2010) also observed that glue-lines were more continuous in areas of the composites where the degree of consolidation of flakes was high and more discontinuous where interparticle contact was poorer.

Quantification of phases in the panels

μCT was used to generate 2-D images of the composites and its component phases. These 2-D images were then used to reconstruct 3-D images of the composites for visualisation and quantification, as well as reveal spatial geometry of the matrix network and other phases. 3-D images enable computation of numerical indices for matrix distribution and its relationship to other phases in the composites (Evans et al. 2010). μCT has the potential to accurately image porous materials and quantify the void and solid phases in the materials. Quantification of the void and solid phases in fibre composites is important because of its prediction on certain properties, such as density which is a determinant of other properties of composites. To determine the relationship between the distribution of fibres, cement matrix and void space in the composite panels, numerical values were derived for the volumes of such phases across three planes of the panel using maximal sphere modelling (Thovert et al. 2001; Evans et al. 2010). The phase volume distribution in a cross section of the panels is presented in Table 7. It was observed that the treatment increased the volumes of the different phases proportionately in bagasse and pine boards. On the contrary, alkali treatment in wattle decreased the volume of the void space and matrix, while it increased the fibre volume (also see Fig. 15b). This resulted in increased density (as seen in Table 6), better interparticle contact and improved strength properties (Fig. 7).

Conclusion

This study revealed that pre-treatment of natural fibres enhanced the fibre surface characteristics which could have improved the fibre-matrix adhesion and subsequently the flexural properties and dimensional stability of the composites. Alkaline treatment of wattle, pine and bagasse resulted in the largest improvements in the properties evaluated. The treatment also influenced the fibre properties as measured by the chemical composition and functional groups in treated and untreated fibres. The study revealed that magnesium phosphate-bonded composite panels had higher strength values and lower water absorption characteristics compared to calcium phosphate-composite panels. 3-D imaging revealed that the phosphate cement matrix is mainly aligned in the same direction as the fibres forming a continuous network. The analysis also revealed that alkaline treatment resulted in the reduction in void spaces and a proportionate increase in solid phases in the composites. This

Table 7 Phase distribution in phosphate-bonded composites produced from untreated- and alkali-treated fibres

Phase distribution	BUN	BAK	PUN	PAK	WUN	WAK
Air	142.89 (9.92)	204.19 (11.43)	148.78 (11.76)	177.79 (10.73)	204.32 (17.12)	148.22 (12.03)
Matrix	654.35 (45.43)	742.43 (41.57)	386.06 (30.51)	577.74 (34.85)	432.27 (36.22)	359.38 (29.17)
Fibres	643.09 (44.65)	839.53 (47.00)	730.68 (57.74)	902.16 (54.42)	556.75 (46.65)	724.26 (58.79)
Total	1440.33	1786.15	1265.52	1657.69	1193.34	1231.86

Percentage distribution of the phases is given in parenthesis increased the composite strength because of increased density and reduced porosity. The study concluded that a mild alkaline treatment of 0.25 M for 1 h and at 60 °C is sufficient to improve the basic properties of phosphate-bonded composite boards made from black wattle, slash pine and bagasse fibres.

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