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Cellulose modified fibres in cement based composites

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ABSTRACT

The objective of the present work is to evaluate the effect of surface modification of cellulose pulp fibres on the mechanical and microstructure of fibre–cement composites. Surface modification of the cellulose pulps was performed with Methacryloxypropyltri-methoxysilane (MPTS) and Aminopropyltri-ethoxysilane (APTS) in an attempt to improve their durability into fibre–cement composites. The surface modification showed significant influence on the microstructure of the composites on the fibre–matrix interface and in the mineralization of the fibre lumen as seen by scanning electron microscopy (SEM) with back-scattered electron (BSE) detector. Accelerated ageing cycles decreased modulus of rupture (MOR) and toughness (TE) of the composites. Composites reinforced with MPTS-modified fibres presented fibres free from cement hydration products, while APTS-modified fibres presented accelerated mineralization. Higher mineralization of the fibres led to higher embrittlement of the composite after accelerated ageing cycles. These observations are therefore very useful for understanding the mechanisms of degradation of fibre–cement composites.

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1. Introduction

Cellulose fibres are widely available in most developing countries from wood or annual plants. They present several interesting advantages particularly their low density, their bio-renewable character and their availability everywhere at modest cost and in a variety of morphologies and aspect ratios. All these properties make them convenient materials for matrix reinforcement, such as polymer composites or fibre–cement applications, as witnesses the significant number of recent reviews and special issue publications [1–4]. The main drawback associated with cellulose fibres in cement application is their durability in the cementitious matrix and also the compatibility between both phases [5]. In fact, the high alkalinity of water in the pore of the cementitious matrix weakens the cellulose fibres, induces their mineralization [6,7] and, consequently, yields to the decay of the composite tenacity in the long term. Moreover, the severe weathering conditions to which the composite is exposed induce water uptake and release of the composite, which results in continuous volume changes of the porous cement matrix and the hydrophilic cellulose fibres cell wall. It has been observed, as a consequence of these cycles of water uptake and release, a loss of adhesion at the fibre and

cement interface, resulting on disjoining of reinforcing elements and degradation of composite mechanical properties [8].

Several approaches were reported on the use of chemical surface treatment on cellulose fibres to reduce their hydrophilic character and improve their adhesion on the matrix [9]. They were all based on exploiting the reactive hydroxyl functions of the fibre's surface through different chemical procedures, such as esterification, etherification, and urethane formation, among many others. The blocking through chemical pathways reduces the number of reactive hydroxyl groups concomitant with the formation of bonds between the cellulose fibres and the cementitious matrix, resulting in the diminution of the water absorption and in improvements of the mechanical properties of the composite.

The use of silane coupling agents is a very well-known practice in glass–fibre based composites and silica-filled polymeric matrices [10]. These chemicals were applied to cellulose fibre-reinforced polymeric composites [11] and carbon fibre-reinforced cement paste [12], as well as in wood fibre–cement materials [13,14]. Although the innovative character of these reports, there is still a relevant lack of information. For instance, the most appropriate silane and the best grafting conditions which ensure a good adhesion between the fibre and the cement matrix and a significant reduction of the fibre's hydrophilic character. Moreover, the stability of the fibre's modification can be questioned under the composites processing conditions, namely, during the de-watering and

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pressing stages. Furthermore and to the best of our knowledge, the effect of the silane modification on the water absorption and porosity of *Eucalyptus* fibre–cement composites has never been previously investigated.

Several attempts have been carried out; among them one procedure involves the use of silane-based bi-functional molecules to graft the fibre surface, in which one of the extremities remains available to bond with the matrix [15]. Blakenhorn et al. [13] and Pehanich et al. [14] reported the improvement of fibre–cement composites durability when using alkyl-alkoxysilane-treated wood fibres. In another study, Xu and Chung [16] described that the silane bridges the fibre's surface, the fumed silica and the cement matrix, yielding denser and stronger composites. Finally, a patent describing the improvement in fibre–cement strength using silane agents, alkoxysilanes, alkyl-alkoxysilanes, halide organosilanes, carboxylated organosilanes and epoxy-alkoxysilanes was recently published [17]. This patent was focused in the improvement of the fibre–cement performance against the humidity.

The objective of the present work is to evaluate the surface modification of cellulose fibres in order to improve their durability into the fibre–cement composites. The current research will also investigate the physical and mechanical performance of cement based composites reinforced with surface modified fibres and the durability of these composites assessed by accelerated ageing tests. As previously established [18], the choice of silane coupling agents is motivated by their mechanism of interaction, and which consists of the formation of a continuous hydrophobic siloxane network, from which the fourth constituent is pointed out to the matrix, thus forming the interfacial bonding. Hence, the aim is to protect the cellulose fibres from water uptake and to improve the quality of the fibre/matrix interface, thus increasing the interaction between them.

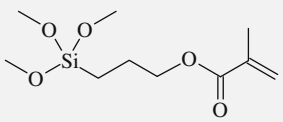
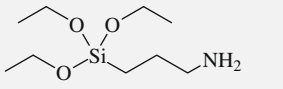
2. Experimental

2.1. Cellulose surface modification and characterization

Conventional bleached eucalyptus kraft pulp was provided by Votorantim Cellulose and Paper, Brazil. The pulp was collected directly from the mill, prior to drying and pressing. It was extensively washed with water and centrifuged to remove any residual chemical from the pulping and bleaching processes.

The procedure used for the surface modification of the cellulose fibres and the choice of the silanes used were based in on the studies developed by Abdelmouleh et al. [18] and Delvasto et al. [19]. The silanes used were methacryloxypropyltri-methoxysilane (MPTS) and aminopropyltri-ethoxysilane (APTS), and their structures are given in Table 1. The silanes/cellulose pulp ratio was 6%, w/w. The silanes were prehydrolysed for 2 h under stirring in 80/20 v/v ethanol–distilled water. Then, cellulose pulp was added to the prehydrolysed silane and the resulting suspension was maintained for 2 h under stirring. At the end of the reaction, the pulp was centrifuged at 1400 rpm for 2 min.

Table 1
The silane coupling agents used in this work.

Silane	Formula
MPTS	
APTS	

To check the efficiency of the surface modification, contact angle measurements were carried out by depositing calibrated droplets of liquid with different polarities on cellulose hand sheets, prepared using a Pulmac ASF–C1 equipment. Table 2 gives the main liquids used in this study and their relevant characteristics in this context. The apparatus used was a dynamic contact angle Data-Physics OCA absorption tester, equipped with a CCD camera working at up to 200 images per second. The dispersive and polar components of the surface energy of the cellulose samples (unmodified, MPTS-modified and APTS-modified) were determined according to the Owens and Wendts [20] approach. Results presented are an average of three experimental data and a maximum standard deviation of about $\pm 2^\circ$.

Cellulose samples used for contact angle measurements were also used for X-ray fluorescence microanalysis with an energy dispersive spectroscopy detector (EDS). The EDS spectra were acquired on an ESEM (ESEM JEOL JSM-6100) apparatus equipped with a back-scattered and secondary electron detector.

The water retention value (WRV) of the pulp was determined according to Tappi UM–256 [21] Standard. It is an empirical measurement of the capacity of the fibres to retain water. It is the ratio of the mass of water retained after centrifugation under specified conditions by a wet pulp samples to the weight of oven-dried (105 °C) initial fibres.

2.2. Composite preparation

Cement based composites were reinforced with unmodified and modified pulp fibres. The cement based composites were molded in 200 mm \times 200 mm plates. They were prepared in laboratory scale using slurry vacuum de-watering followed by pressing technique, as described in details by Savastano Jr. et al. [22].

Fibre–cement formulation was based on previous study [23]. The suspensions were prepared using the following constituents (percentage in dry mass): 5% of pulp (eucalyptus kraft bleached), 77.2% of ordinary Portland cement (OPC) CPV-ARI [24] and 17.8% of ground carbonate. Pulp was dispersed in distilled water by mechanical stirring at 3000 rpm for 5 min to disaggregate the fibres prior to cement addition. The mixture formed with approximately 20% of solids was then stirred at 1000 rpm for an additional 4 min. The slurry was then transferred to the casting box and the vacuum applied (approximately 80 kPa gauge), to evacuate water until a solid surface is obtained. The pads were then pressed at 3.2 MPa for 5 min, wet sealed in a plastic bag to cure at room temperature for two days and further immersed into water for 26 days. The prepared pads were wet cut into four 165 mm \times 40 mm flexural test specimens using a water cooled diamond saw. Specimen thickness was approximately 5 mm. Eight fibre–cement samples were used for each condition. After the completion of the water immersion curing stage, the specimens were tested on the 28th day after production. The specimens were soaked in water for 24 h, under saturated condition, prior to mechanical tests.

Table 2
Contact angle measurement probes and their characteristics.

Probe	Surface tension (mJ/m ²)		
	Dispersive	Polar	Total
1-bromonaphthalene	44.6	0	44.6
Ethylene glycol	29.0	19.0	48.0
Diiodomethane	48.5	2.3	50.8
Glycerol	37.0	26.4	63.4
Water	21.8	51.0	72.8

2.3. Soak and dry accelerated ageing cycles

The soak and dry accelerated ageing cycles involved comparative analysis of the physical and mechanical performance of the composites, before and after this test. Composites were successively immersed into water at $20\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ for 170 min, after resting for 10 min, they were heated to a temperature of $70\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ for 170 min in a ventilated oven. An interval of 10 min (at room temperature) is usual prior to beginning the next cycle, as recommended by EN 494 [25] standard. Each soak and dry set represents one cycle, which was repeated 200 times, i.e., 200 ageing cycles. This method simulates natural ageing in severe conditions, although additional studies are needed to determine the most relevant accelerated conditions corresponding to natural weathering, in order to predict more precisely the long-term behaviour of the composites produced.

2.4. Mechanical, physical and microstructural characterization of the fibre–cement composites

Mechanical tests were performed using the universal testing machine Emic DL-30,000 equipped with 1 kN load cell. Four-point bending configuration was employed to evaluate the limit of proportionality (LOP), the modulus of rupture (MOR), the modulus of elasticity (MOE) and the toughness (TE) of the specimens. A 135 mm span and a deflection rate of 1.5 mm/min were adopted in the bending tests, in order to determine the LOP, MOR and MOE, following calculations specified in Eqs. (1)–(3).

$$\text{LOP} = \frac{P_{\text{lop}} \cdot L_v}{b \cdot h^2} \quad (1)$$

$$\text{MOR} = \frac{P_{\text{max}} \cdot L_v}{b \cdot h^2} \quad (2)$$

$$\text{MOE} = \frac{276 \cdot L_v^3}{1296 \cdot b \cdot h^3} \cdot m \quad (3)$$

where P_{lop} is the load at the upper point of the linear portion of the load vs. deflection curve, P_{max} is the maximum load, L_v is the major span, b and h are the specimen width and depth respectively, m is the tangent of the slope angle of the load vs. deflection curve during elastic deformation.

Toughness (TE) was defined as the energy absorbed during the flexural test divided by the cross-sectional area of the specimen under investigation (Eq. (4)), as described previously [23] and adapted from RILEM [26]. The absorbed energy was obtained by integration of the area below the load vs. deflection curve at the point corresponding to a reduction in load carrying capacity to 30% of the maximum reached. The deflection during the bending test was collected by the deflectometer positioned in the middle span, on the down side of the specimen. The values of stress (σ) were calculated using the Eq. (1) for each load value, P . The values of deflection were divided by a span of 135 mm and called specific deflection (δ), in the present work. The specific deflection at the end of each test (when σ decreased to $0.3 \times \text{MOR}$) was called final specific deflection (δ_{final}) and was compared for each composite. Fig. 1 presents a typical stress vs. specific deflection curve, which defines LOP, MOR, toughness (TE) and the final specific deflection used in the present work. MOE was not defined in Fig. 1 because it was determined by Eq. (3) using load vs. deflection curves.

$$\text{Toughness} = \frac{\text{absorbed energy}}{b \cdot h} \quad (4)$$

Water absorption (WA), apparent void volume (AVV) and bulk density (BD) values were obtained from the average of six specimens for each design, following the ASTM C 948–81 [27] Standard.

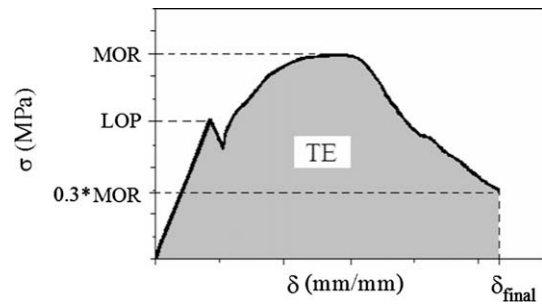


Fig. 1. Definition of the mechanical parameters in a typical stress vs. specific deflection curve.

Scanning electron microscopy (SEM) was applied for the characterization of the fibre–matrix interface and the transition zone. A back-scattered electron (BSE) detector was applied to observe the morphological features of cut and polished surfaces. The BSE imaging permits the easy identification of cementitious phases since electron scattering goes with the atomic number. Dark and light areas are related to lighter and heavier elements, respectively. Energy Dispersive Spectrometry (EDS) analyses were performed in order to localize the carbon (C), calcium (Ca) and silicon (Si) atoms on the same polished surface specimens. The preparation of specimens for BSE and EDS was accomplished with vacuum (25 kPa gauge) impregnation using epoxy resin (MC-DUR1264FF). BSE EDS samples were ground with silicon carbide (SiC) grinding paper with sequential grit sizes of 120, 320 and 500 for 4 min each, using ethanol (Struers DP-lubricant), as lubricant. A final polishing was carried out using sequentially 8–4 μm , 4–2 μm and 1–0 μm diamond polishing compound during 6 min each. Polished samples were carbon coated before being analyzed in a LEO Leika S440 electronic microscope with an acceleration voltage of 20 kV and a current of 150 mA, as described elsewhere [28].

3. Results and discussion

3.1. Characterization of fibre modification

APTS-modified pulps presented higher water retention value than unmodified and MPTS-treated pulps (Fig. 2). This result can be explained by higher hydrophilic character of the APTS-modified fibres, therefore justifying the use of microscopic and surface energy evaluation. Fig. 3 presents the EDS spectra of the cellulose samples. Despite the small intensity, the characteristic X-ray emission peak of the Si was detected on the surface of the modified samples, which gives evidence about the occurrence of the grafting with the two silanes used. Indeed, taking into account that the X-

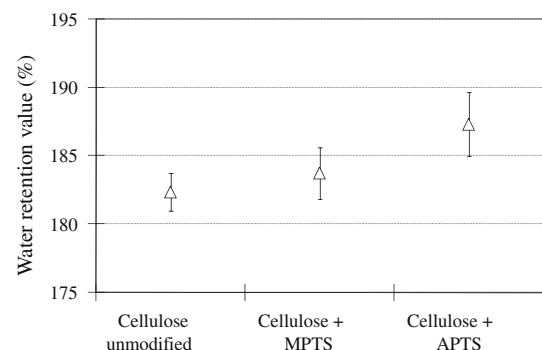


Fig. 2. Average water retention value and standard deviation of the unmodified and MPTS- and APTS-modified cellulose pulps.

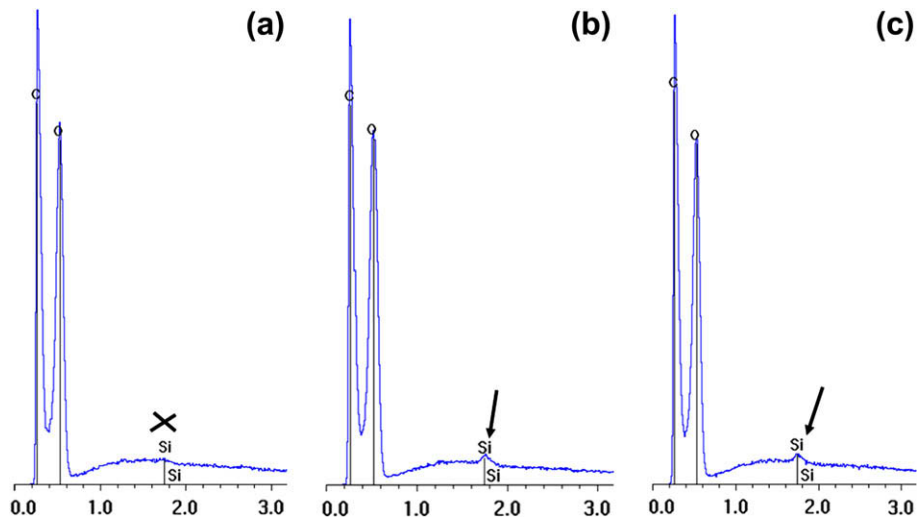


Fig. 3. Energy dispersive spectrometry (EDS) of (a) unmodified, (b) MPTS- and (c) APTS-modified cellulose samples.

ray counted comes from less than 1 μm depth in the material the small intensity of the Si peak as regarding the C and O $\kappa\alpha$ emission peaks suggest the silanes are distributed on the surface of the fibres and do not form a hybrid silicate-cellulose composite. Composite formation would lead to formation of a sesquisiloxane layer with fibres dispersed inside, then the majority of X-rays would come from the sesquisiloxane layer and much more intense Si/C would be observed. It is important to note that silicon was not detected on blank (unmodified) samples which were not exposed to silane coupling agents. No information could be obtained on silane thickness layer or silane coverage degree from the EDS measurements.

Fig. 4 presents the polar and dispersive contributions to the surface energy of unmodified and modified pulps. Virgin fibres presented quite low polar contribution to the surface energy, which can be attributed to surface contamination of the pulps by remaining extractives and lignin fragments, as reported elsewhere [9,29]. The modification of the pulp with APTS increased the surface energy of the fibres, due mainly to the increment in the polar component. This increase is associated to the presence of amine groups which increase in meantime the hydrophilic character with possibility of hydrogen bonds with water. It is also probable that the modification conditions give rise to the fibre's surface purification (extraction of lignin and other constituents) and consequently an increase in the polar component of the surface energy [9,29]. The hydrophilic nature of diaminofunctional silane was also reported by Xu and Chung [16]. MPTS-modified fibres presented surface en-

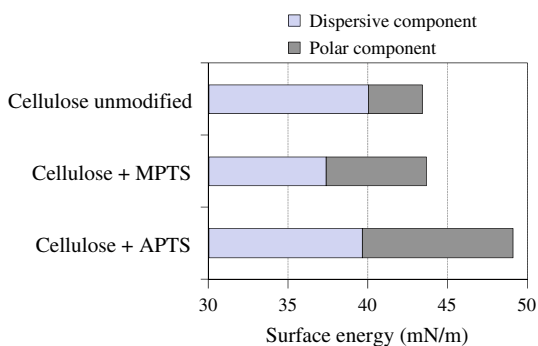


Fig. 4. Surface energy components (polar and dispersive) of the unmodified and modified cellulose fibres.

ergy similar to that of unmodified fibres. Since fibre modification was evidenced by EDS, the low polarity of the MPTS-modified fibres is explained by the surface orientation of the MPTS group on fibre surface. MPTS reacts with cellulose fibres by the formation of Si–O–C bonds or the formation of a network of Si–O–H...O–C hydrogen bonds once hydrolysed silanes (silanol groups) adsorb on the fibres surface [30]. If the methacrylate groups are oriented with the ester ending toward the water–fibre interface, the surface of the fibre would show a quite hydrophilic group which could explain the low surface energy and the high contact angles for polar liquids.

3.2. Effect of fibre modification on the mechanical and physical performance of the fibre-reinforced composites

Table 3 shows the effect of pulp modification and accelerated ageing in the mechanical performance of the composites. After 28 days of cure, composites reinforced with APTS-modified fibres presented higher MOR value than those associated with composites made of unmodified and MPTS-modified pulps. The toughness (TE) of the composites after 28 days of cure was not influenced by the modification with silane coupling agents; however the final specific deflection (δ_{final}) values of unmodified and MPTS-treated fibre-reinforced composites were higher than those linked to the composite reinforced with APTS-modified fibres (Fig. 5). LOP values seem to be not influenced by the fibre modification and by the accelerated ageing cycles. As reported in the previous section, it is probable that the fibre modification conditions give rise to fibre's surface purification (extraction of lignin and other constituents), which increased the MOE values of the composites after 28 days of cure due to the increase of fibre to matrix adherence. Accelerated ageing increased the MOE values, which is a consequence of densification and continued hydration of the cement phase of the composite caused by the soak and dry cycles.

Fig. 5 shows the effect of accelerated ageing on the consistent reduction of the final specific deflection. Figs. 6 and 7 depict the differences between the typical stress vs. specific deflection curves of the composites after 28 days and after 200 ageing cycles, respectively. The average MOR and toughness (TE) values, and final specific deflection significantly decreased after 200 ageing cycles for all the composites, compared to those corresponding to 28 days of curing. The decrease of toughness and final specific deflection is due to the densification of the fibre–matrix interface, which improved fibre to matrix bonding and consequently led to fibre rup-

Table 3

Average values and standard errors of the limit of proportionality (LOP), modulus of rupture (MOR), modulus of elasticity (MOE), toughness (TE), water absorption (WA), apparent void volume (AVV) and bulk density (BD) of the fibre–cement composites.

Fibre condition	Composite condition	LOP (MPa)	MOR (MPa)	MOE (GPa)	TE (kJ/m ²)	WA (%)	AVV (%)	BD (g/cm ³)
Untreated	28 days	6.9 ± 1.1	9.9 ± 1.4	13.3 ± 1.2	0.86 ± 0.25	16.4 ± 0.9	29.0 ± 1.0	1.77 ± 0.04
MPTS		6.5 ± 1.0	10.7 ± 1.3	16.3 ± 1.7	0.83 ± 0.46	17.7 ± 1.3	30.8 ± 1.5	1.75 ± 0.04
APTS		7.8 ± 1.3	12.1 ± 1.4	16.3 ± 2.5	0.82 ± 0.29	16.7 ± 0.8	29.9 ± 1.0	1.79 ± 0.03
Untreated	200 cycles	6.3 ± 0.9	7.5 ± 0.5	17.7 ± 1.1	0.13 ± 0.07	15.2 ± 1.2	26.5 ± 1.9	1.75 ± 0.03
MPTS		7.2 ± 0.9	8.0 ± 1.0	18.6 ± 4.6	0.30 ± 0.12	16.2 ± 1.7	27.9 ± 2.4	1.72 ± 0.08
APTS		6.9 ± 1.7	8.3 ± 1.0	18.4 ± 3.8	0.13 ± 0.07	13.5 ± 0.5	24.6 ± 0.7	1.83 ± 0.03

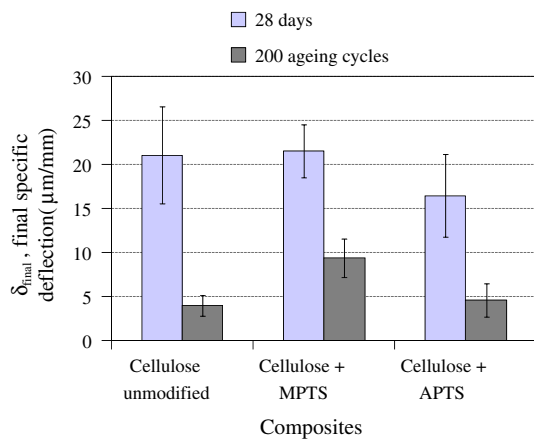


Fig. 5. Average values and standard deviation of final specific deflection (δ_{final}) in bending tests for the fibre–cement composites after 28 days of curing and after 200 ageing cycles.

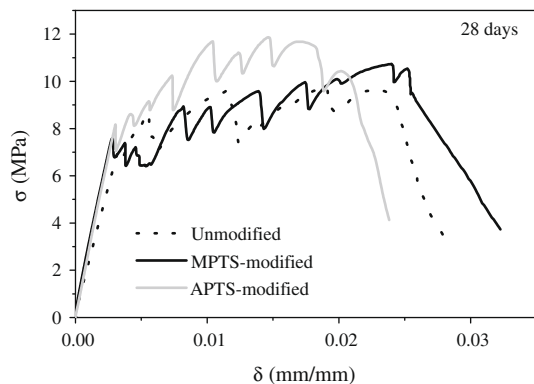


Fig. 6. Typical stress vs. specific deflection curves of the fibre–cement composites (with unmodified, MPTS- and APTS-modified fibres) after 28 days.

ture instead of fibre pull-out. After ageing tests, differences in MOR were not observed between composites made with unmodified and modified fibres indicating that the composite degradation took place no matter what treatments were applied to the fibres. However, after 200 ageing cycles, MPTS-modified fibre-reinforced composites presented higher toughness (Table 3) and final specific deflection (Fig. 5), than those of the other two composites. This behaviour can be understood by the lower mineralization of MPTS-modified fibres compared to the others as described in Section 3.3.

The effect of fibre modification on the physical properties of the composites is presented in Table 3. Significant differences were not observed between the composites with unmodified and those based on modified fibres, after 28 days of curing. Nevertheless, after 200 ageing cycles, composites with APTS-treated fibres pre-

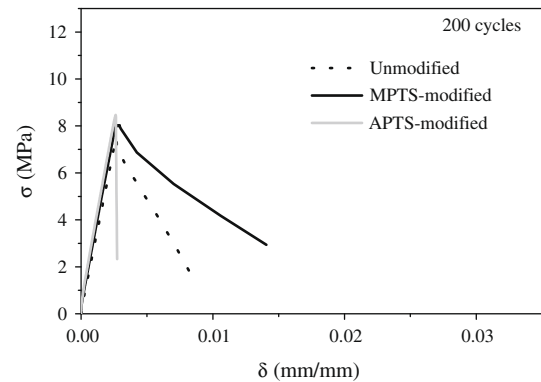


Fig. 7. Typical stress vs. specific deflection curves of the fibre–cement composites (with unmodified, MPTS- and APTS-modified fibres) after 200 cycles.

sented lower water absorption and apparent porosity, to compare with materials made with unmodified and MPTS-grafted fibres. The bulk density of the composites with APTS-modified pulps showed a tendency of higher results in comparison to other composites that showed lower bulk density. This ageing dependence behaviour indicates different organic–inorganic interaction pattern in the composites. Low surface energy fibres would suffer slow disjoining and increase the porosity while high surface energy would slowly promote intimate contact between fibres and cement materials. Indeed, the higher surface energy of the APTS-modified fibre permits higher interaction with the cementitious matrix, thus diminishing fibre–matrix debonding and decreasing of the porosity in the composite. Xu and Chung [16] also reported the lower porosity of composites reinforced with silane-treated (mixture of N-(β-aminoethyl)-γ-aminopropyltri-methoxysilane and γ-glycidoxypropyltri-methoxysilane) carbon fibres. The authors attributed this behaviour to the hydrophilic character of the silane used, which improved the fibre–matrix bonding. As presented in the next section (Fig. 8b), the APTS-modified fibres are filled with cement hydration products (rich in calcium), which also explain the diminution in the porosity of composites (Table 3).

3.3. Effect of fibre modification on the microstructure of the fibre-reinforced composites

Fig. 8 shows the SEM micrographs of composites after 28 days of curing and reinforced with unmodified and silane modified fibres. Dark areas in the image (due to low atomic number) pertain to cross or longitudinal sections of the fibres. It was observed that the majority of the unmodified (Fig. 8a and b) and APTS-modified fibres (Fig. 8c and d) present the lumen cavity filled with cement hydration products (light grey colour). These fibres do show evidence of ettringite/monosulphate and calcium hydroxide (CH) formation within the fibre lumen. This is particularly evident in the EDS spots (1–7 in Fig. 8), where calcium is the predominant element observed within the fibre lumen. During the curing by

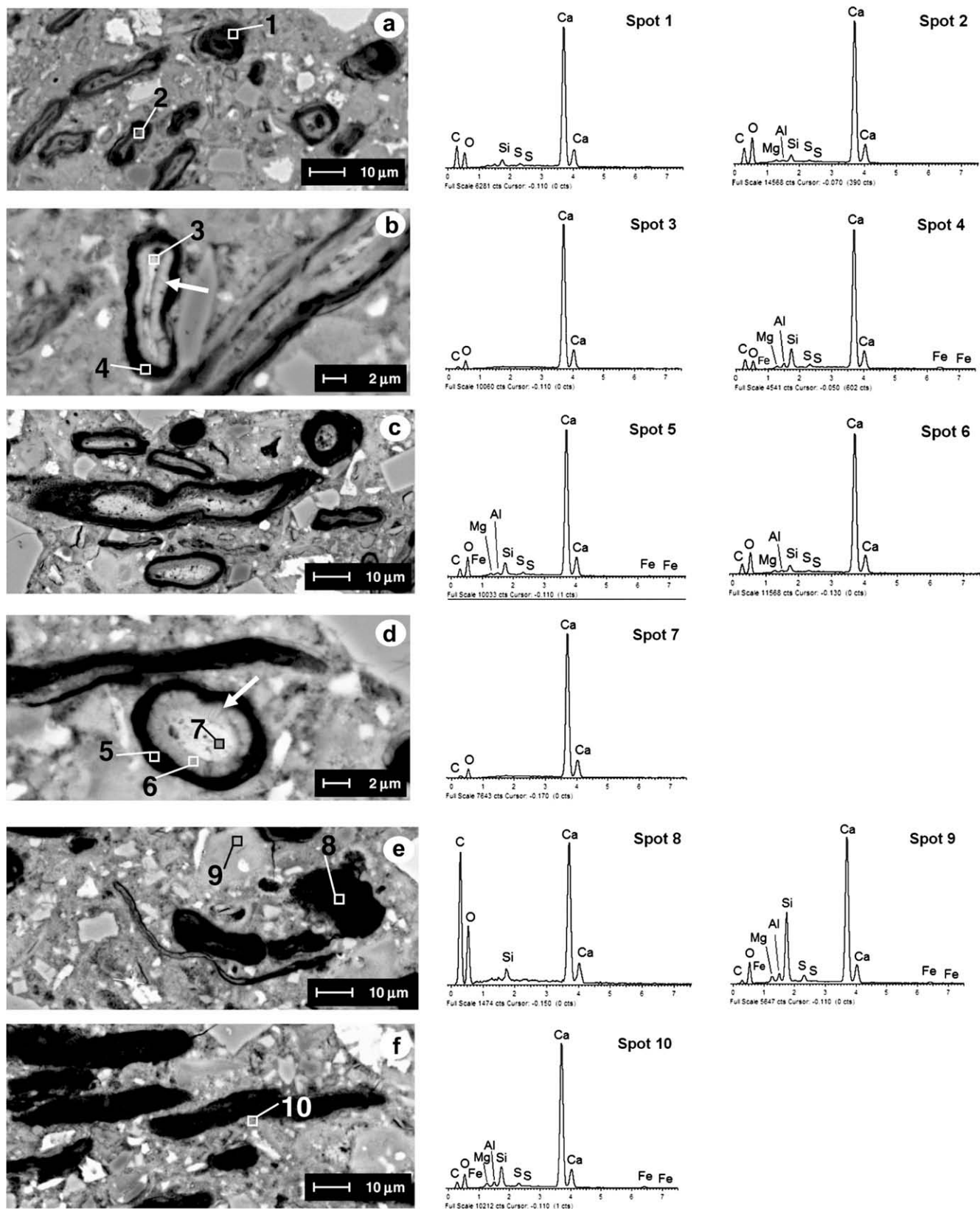


Fig. 8. SEM BSE images of the polished cross-section surfaces of composites reinforced with: (a and b) unmodified; (c and d) APTS-modified fibres; and (e and f) MPTS-modified fibres. Images obtained after 28 days of curing. EDS spot analyses are signalized in the images (spots 1–10).

immersion into water, the free ions from the dissolution of OPC phases penetrated into the fibre lumen, leading to the formation of ettringite/monosulphate and calcium hydroxide (CH). Batic

et al. [31] have shown that the re-precipitation of ettringite in microcracks and voids of cement paste can occur under normal (i.e., room temperatures) curing conditions. Secondary ettringite

formation has been previously suggested as one of the degradation mechanisms of pulp fibre into cement matrix [32,33]. As observed in Fig. 8a, one step of the fibre mineralization seems to be the formation of ettringite/monosulphate layers in the inner boarder of the lumen cavity. Arrows in Fig. 8b and d illustrates the formation of needle-like crystals, believed to be ettringite based on the EDS data. The same observation was reported by Mohr et al. [33] for kraft fibres after 2 wet/dry cycles. Based on these visual observations (arrows in Fig. 8a and b), the typical needle-like ettringite appears to be formed perpendicularly to the inner lumen surface. The re-precipitation of calcium hydroxide (CH) was observed in the centre of the lumen cavity, surrounded by the ettringite layers into the unmodified and APTS-modified fibres (Fig. 8b and d). In the case of CH re-precipitation, mainly calcium was detected on the EDS spots (spots 3 and 7).

In the MPTS-modified fibre-reinforced composites, the majority of the fibres are not filled with hydration products of the cement, indicating that MPTS sesquisiloxane macromolecules formed during hydrolysis in solution and adsorbed on the surface of the cell wall fibres acts as a barrier to the aqueous solution. Its presence prevents re-precipitation of mineral phases within the fibre cell wall minimizing fibre mineralization by interpenetration of cement hydration products. The amount of carbon (C) in the cell wall of the unmodified (spot 1 and 4 in Fig. 8) and APTS-modified fibres (spot 5 in Fig. 8) is lower than that observed to MPTS-treated ones (spot 8 in Fig. 8). In this case, it is believed that the hydration products of the cement were deposited mainly around the fibres (Fig. 8e and f). The EDS spots (spots 9 and 10 in Fig. 8) show the sulphate-rich phases (e.g., ettringite and monosulphate) around the fibres.

Soak and dry cycles result also in alkali leaching from Portland cement pulp fibre–cement composites [33,34]. According to these authors, CH re-precipitation is a dominant step in the degradation of kraft pulp fibre–cement composite during wet/dry cycles. In the present work, after 200 ageing cycles, in the composites with MPTS-modified fibres (Fig. 9a and b) the CH re-precipitation was reduced or prevented. The lumens of the fibres were still not filled with hydration products of the cement (rich in calcium – light colour), which led to higher toughness and final specific deflection

(Table 3 and Fig. 5, respectively), than composites with unmodified and APTS-treated fibres, after 200 ageing cycles. Composites reinforced with unmodified and APTS-grafted fibres presented lower toughness due to the re-precipitation of ettringite/monosulphate and CH into the fibre's lumens (Fig. 9c and d), as previously discussed, and therefore embrittlement of the composite.

Finally, in the EDS atomic mapping of the calcium atoms of the polished surfaces corresponding to APTS-modified fibres reinforced composites, calcium (green) is located within the fibre cell wall (Fig. 9d). The concentration of carbon (red) decreased in the fibre cell wall. In the composites reinforced with MPTS-modified fibres, the carbon atoms are still present in great amount within the fibre cell wall (Fig. 9b). Thus, MPTS modification of the fibres seems to play an important role in minimizing the degradation and embrittlement of the fibres during curing and soak and dry cycling.

4. Conclusion

The surface modification of the fibre carried out in this work showed significant influence on the microstructure of the composites (fibre–matrix interface and mineralization of the fibre lumen). Results obtained with measurements of wettability indicated differences between the two modified fibres with hydrophilic APTS-modified fibres and less hydrophilic MPTS-modified fibres. The consequence of these different graftings has been observed in the microstructure of the composites. Composites with unmodified and APTS-modified fibres showed that the lumens were filled with cement hydration products (known as the mineralization of the cellulose fibres), thus improving the adhesion between organic and inorganic materials after exposition to accelerated ageing tests. Instead, the MPTS-grafted fibres did not display lumens filling. These observations point out that modifying surface energy of the fibres is a valid approach to monitor the adhesion between cellulose pulp fibres and cementitious matrix. Accelerated ageing cycles decreased MOR and toughness of the composites indicating the degradation of the composites no matter the treatment initially applied to the cellulose pulp. Non mineralized filaments in composites with MPTS-modified fibres led to less damage in toughness

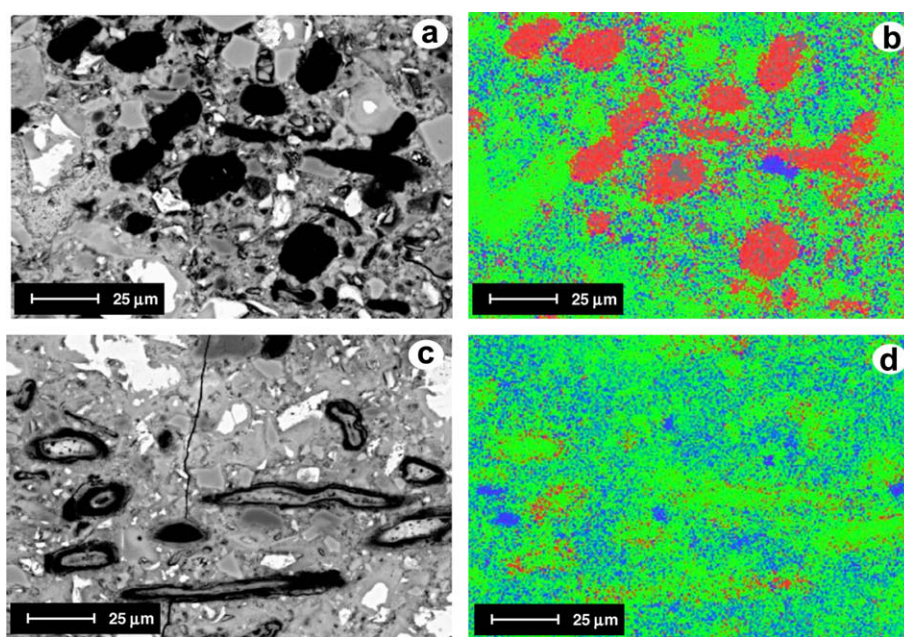


Fig. 9. SEM BSE images and atomic mapping of C (red), Ca (green) and Si (blue) of the polished surfaces of composites reinforced with: (a and b) MPTS-modified fibres and (c and d) APTS-modified fibres. Images obtained after 200 accelerated ageing cycles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and in final specific deflection after accelerated ageing than in the other composites. These results are very interesting for ongoing research in the direction of other fibre modification strategies, and for understanding the major mechanisms that influence the degradation of mechanical performance of the cellulose fibre–cement materials.

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