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Processing and dimensional changes of cement based composites reinforced with surface-treated cellulose fibres

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ABSTRACT

The objective of the present work is to evaluate the impact of the surface grafting of cellulose fibres on the processing, dimensional stability and mechanical performance of fibre–cement composites. The surface modification of the pulps was performed with methacryloxypropyltri-methoxysilane (MPTS), aminopropyltri-ethoxysilane (APTS) and n-octadecyl isocyanate, an aliphatic isocyanate (AI). X-ray photoelectron spectroscopy (XPS) showed that the chemical changes have indeed occurred at the surface, and contact angle measurements showed that the surface energy has also changed. MPTS- and AI-treated fibres presented lower hydrophilic character than untreated fibres, whereas APTS increased the water retention value of the pulp. MPTS-treated fibres decreased the water retention and improved dimensional stability of the fibre–cement composites, while the contrary occurred with other modified fibres. Fibre–cement strength was little influenced by fibre treatment, whereas AI-treated fibres contributed to higher specific energy (SE) and the lower SE value for APTS-treated fibres is an indication of the improvement on fibre to cement adherence. These results are promising and contribute toward new strategies to improve the processing and stability of natural fibre-reinforced cement products.

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, bio-renewable character and wide availability at modest cost and in a variety of morphologies. These attributes make them convenient materials for matrix reinforcement, such as for polymer composites or fibre–cement applications, as witnessed by the significant number of recent reviews and special issue publications in this subject area [1–5].

Fibre–cement products have been widely used in the world as corrugated or flat roofing materials, cladding panels and water containers, in a large number of building and agriculture applications [6,7]. The main reason for incorporating fibres into the cement matrix is to improve the toughness, tensile strength, and the cracking deformation of the composite. Another reason for using fibres is their capacity of solids retention during processing of the composites produced by the Hatschek process, which is the most widely employed one in producing fibre–cement components [8]. One of the drawbacks associated with cellulose fibres in cement application is their dimensional instability when submitted to changing relative humidity (RH) atmospheres. This instability is promoted by: (i) the water sensitivity of cellulose fibres, and (ii) the effects of carbonation, high alkali content of the cement matrix, and generation of incompatible stresses [9,10]. The conditions to which the composite is exposed under weathering induce its water uptake and release. These variations result in continuous volume changes of the porous cement matrix and hydrophilic cellulose fibres cell wall. As a consequence, there is a loss of adhesion at the fibre/cement interface and an increase of micro- and macro-cracks, which contributes to strength decay and loss of durability of the fibre–cement composite [11–13].

Fibre dispersion and fibre water absorption are crucial in the industrial process. They influence the ease with which fibre–cement is handled at fresh state and can also affect hardened state properties. The dispersion and the water absorption impact mainly the mineral fines retention, dewatering or composite formation and, as a consequence, on the overall efficiency of the Hatschek machine. The high water absorption of the fibre prejudices the on-line processing of the green sheet, known informally by the operator as: low drainage rates or "elephant skin" appearance. Indeed, usually, the appearance of such a phenomenon is visible when the green sheet has high humidity content [14]. Contrarily,

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if the humidity is very low, then delamination occurs, being more problematic and usual for suspensions with a low amount of fine particles [14] or when very low drainage rates occur. These are key issues for the industry and there is a serious lack of available published literature on the subject. The final water content in the green sheet composite also impacts the mechanical performance: the lower the final water/cement ratio the better the mechanical properties of the fibre–cement composites.

Several approaches were reported on the use of chemical surface treatments on cellulose fibres to reduce their hydrophilic character and improve their adhesion to the matrix [15,16]. 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 reduction of hydroxyl groups results in the diminution of the water absorption and in the improvements of the mechanical properties of the composite.

The use of silane coupling agents is a well-known practice in glass-fibre based composites and silica-filled polymeric matrices [17]. These chemicals were applied to cellulose fibre-reinforced polymeric composites [18] and carbon fibre-reinforced cement paste [19], as well as in wood and non-wood fibre–cement-based materials [7,20–22]. Blankenhorn et al. [20] and Pehanich et al. [21] reported the improvement of fibre–cement composites durability when using alkyl-alkoxysilane-treated wood fibres. In another study, Xu and Chung [23] described that the silane bridges the fibre's surface, the fumed silica and the cement matrix, yielding denser and stronger composites. Another successful approach for fibre hydrophobization involves the reaction of aliphatic isocyanates on the cellulose surface [24] and their impact on the fibre based polymer bio-composites have been studied recently [25]. However, there is still a relative lack of relevant information in the literature. For instance, the best grafting conditions that ensure good adhesion between the fibre and the cement matrix and a significant reduction of the fibre's hydrophilic character have not been presented. Moreover, the stability of the fibres modification can be questioned under the composites processing conditions, namely, during the de-watering and pressing stages. Furthermore and to the best of our knowledge, the effects of the silane and isocyanate treatment on the processing, water absorption and dimensional stability of eucalyptus fibre–cement composites have not been previously reported.

The objective of the present work is to evaluate the surface modification of cellulose fibres in order to improve processing, dimensional stability and mechanical performance of fibre–cement composites. The current research will also investigate the quality of the cellulose fibre grafting by XPS.

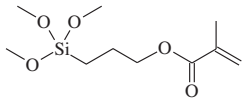
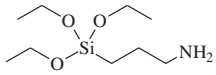
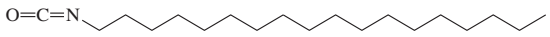
2. Experimental

2.1. Materials

Conventional bleached and unrefined eucalyptus kraft pulp with average fibre length of 0.81 ± 0.01 mm, and average fibre width of 15.9 ± 0.3 μm, was used in the experiments. The silanes and the aliphatic isocyanate used for the surface modification of the cellulose fibres were methacryloxypropyltri-methoxysilane (MPTS), aminopropyltri-ethoxysilane (APTS) and n-octadecyl isocyanate (AI) respectively. The choice of the chemical reagents is based on the successful surface modifications achieved by their use, as reported in previous studies [7,23]. Their chemical structures are given in Table 1.

High initial strength ordinary Portland cement (OPC) CPV-ARI [26] and ground carbonate material (GCM) were used as the matrix of the fibre–cement composites. Ground carbonate material (GCM) was used as a partial substitution of OPC, in order to reduce costs concerning the fibre–cement production. Oxide compositions of the OPC and of the GCM were accomplished by X-ray fluorescence (XRF) spectrometry (PANalytical Axios-Advanced). Oxide compositions of the OPC and of the GCF are presented in Table 2. Particle size distribution by laser granulometry (Malvern Mastersizer S long bed, version 2.19) was performed using ethanol as a dispersion medium. According to particle size distribution, 50% of the particles are smaller than 11.0 μm and 16.2 μm, for OPC and ground carbonate material respectively. Most of particles (90%) are smaller than 27.3 μm and 64.4 μm, for OPC and GCM respectively.

Table 1
Chemical structures of the silane and isocyanate coupling agents.

Reagents	Formula
MPTS	
APTS	
AI	

2.2. Surface chemical treatment of the cellulose fibres

Before the surface treatment, the cellulose fibres were soxhlet-extracted with ethanol during 6 h to remove surface contaminants that may disturb the adequate grafting of the chemical reagents onto the cellulose surface [27]. After that, the fibres were air-dried to constant weight.

The concentration of the selected silane was 0.05 mol/L of ethanol–distilled water (80/20 v/v) mixture. It was chosen based on the adsorption isotherms previously established [28]. The silanes were pre-hydrolysed for 2 h under stirring in the ethanol–distilled water mixture, at room temperature. Then, cellulose pulp was added to the reactive pre-hydrolysed silane and the 2.5% w/w cellulose resulting suspension was maintained for 2 h under stirring. At the end of the reaction, the pulp was filtered and the fibres were immediately heat-treated at 110 °C for 12 h, in order to promote the actual chemical coupling. MPTS- and APTS-treated fibres were submitted to 6 h soxhlet extraction with dichloromethane, in order to remove the physically adsorbed molecules at the fibre surface, before being subjected to the surface characterisation.

The AI-treatment was carried out in a three-necked round-bottomed flask, equipped with a reflux condenser, which contained 3.5% w/w of cellulose suspension in toluene. The system was kept under a nitrogen atmosphere. An excess of n-octadecyl isocyanate (~18% w/w of the suspension) was slowly added (drop by drop) when the reaction temperature reached 90 °C. At the end of the AI addition, the temperature was increased up to 110 °C and the reaction was prolonged for 30 min. The modified fibres were filtered and washed with ethanol to remove the excess and the

Table 2
Oxide composition (% by mass) of the cement (OPC) and of the ground carbonate filler (GCF).

	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	SO_3	MnO	P_2O_5	TiO_2
OPC[a]	63.5	3.1	19.4	4.1	2.3	0.2	1.1	3.0	–	–	–
GCM[b]	39.1	8.9	9.0	2.2	1.2	0.1	0.4	–	0.1	0.2	0.1

[a] Loss of ignition (1000 °C) = 3.3% in mass.
[b] Loss of ignition (1000 °C) = 38.7% in mass.

unreacted AI, as reported elsewhere [24]. Finally, after 6 h soxhlet extraction with ethanol to remove unbounded and physically adsorbed molecules, the AI-treated fibres were air dried before the surface characterisation.

2.3. Fibre characterisation

2.3.1. XPS spectroscopy

XPS experiments were performed using a XR3E2 apparatus (Vacuum Generators, UK) equipped with a non-monochromated Mg Kα X-ray source (1253.6 eV) and operated at 15 kV under a current of 20 mA. Samples were placed in an ultrahigh vacuum chamber (10^{-8} mbar) with electron collection by a hemispherical analyser at an angle of 90°. Signal decomposition was performed using Spectrum NT, and the C1s signal was shifted to ensure the C—C/C—H signal of the decomposition occurred at 285.0 kV. Comparison of the elementary surface composition was performed using:

$$\frac{I_1/s_1}{I_2/s_2} \tag{1}$$

where I_i is the intensity of the signal i (carbon, oxygen, silicon or nitrogen) and the s_i is the atomic sensitivity factor.

2.3.2. Contact angle measurements and surface energy

Contact angle measurements were carried out by depositing calibrated droplets of liquids with different polarities on cellulose hand sheet surfaces in order to check the efficiency of the surface modification. The liquid probes used were: 1-bromonaphtalene, ethylene glycol, diiodomethane, glycerol and water; and their relevant characteristics in this context were reported in Tonoli et al. [29]. The apparatus used was a dynamic contact angle DataPhysics OCA absorption tester, equipped with a CCD camera working at up to 200 images/s. The dispersive and polar components of the surface energy of the cellulose samples (untreated, MPTS-treated, APTS-treated and AI-treated) were determined according to the Owens and Wendts [30] approach (where the work of adhesion is replaced by the Young–Duprès equation):

$$\gamma_L(1+\cos\theta) = 2\sqrt{\gamma_L^D\gamma_S^D} + \sqrt{\gamma_L^P\gamma_S^P} \tag{2}$$

with γ, γ^D, and γ^P being the total, dispersive, and polar surface energy respectively. Subscripts L and S refer to the liquid drop (L) and the solid surface (S) respectively, and θ denotes the contact angle between the solid substrate and the liquid drop. The presented results are the average of three experimental measurements. The maximum standard deviation was about ±3°.

2.3.3. Water retention value

The water retention value (WRV) of the untreated and treated pulps was determined according to Tappi UM-256 [31] Standard. It is an empirical measurement of the capacity of the fibres to retain water, and it was calculated by the ratio of the mass of water retained by pulp samples after centrifugation (at a speed that gives the centrifugal force of 900 G) for 30 min, and that of oven-dried (105 °C) initial fibres.

2.3.4. Fibre bonding index

The fibre intrinsic strength and fibre bonding index were measured in a zero-span tester Pulmac Z2400-C1 according to standard methods of Tappi T 273 cm-95 [32] and T 231 pm-96 [33]. The fibre bonding index, as opposed to fibre intrinsic strength, is measured using dry cellulose hand sheets, and is an indicative measurement of the interfibre bond-forming capacity or cohesiveness of the fibres. Higher value of fibre bonding index is a sign of the improvement in hydrogen bonding between the fibres.

2.4. Production of the fibre–cement composites

Cement based composites were reinforced with untreated and treated pulp fibres. Cement based composites were moulded in 200 mm × 200 mm plates, prepared in laboratory scale using slurry vacuum de-watering/pressing technique, as described in details by Savastano Jr. et al. [34].

Fibre–cement formulation was based on previous studies [29,35]. The suspensions were prepared using the following constituents (percentage by dry mass): 5% of pulp (untreated or treated cellulose fibre), 77.2% of ordinary Portland cement (OPC) CPV-ARI [26] and 17.8% of ground carbonate. The correspondent percentage of cellulose pulp in volume of the solids is around 9%. The pulp was dispersed into 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 period of 4 min. The slurry was then transferred to the casting box and the vacuum applied (approximately 80 kPa gauge) during around 2.5 min, 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 2 days and immersed into water for 26 days. The prepared pads were wet cut into four 165 mm × 40 mm bending test specimens using a water cooled diamond saw. The specimen thickness was approximately 5 mm. Five fibre–cement samples were used for each condition. After the completion of the water immersion curing stage, the specimens were tested 28 days after production.

2.5. Process parameters of the fibre–cement composites

The effect of the fibre treatment on fibre–cement composites processing was evaluated. The moisture of the green composite sheets reinforced with the different fibres was calculated before being pressed at 3.2 MPa. In fact, the quantity of water retained after the drainage process, expressed as a percentage of the total mass of the specimens, was measured. This parameter consisted of establishing the difference between the weights before and after pressing at 3.2 MPa and corresponded to the quantity of water removed during pressing cycle.

The thickness of the green sheet under and after pressing at 3.2 MPa were measured in order to determine the spring effect induced by water uptake and release of the fibres when submitted to negative and positive pressures, respectively. Such an experiment aimed simulating the condition that the green sheet suffers during the action of the cylinder former in the Hatschek process. Such parameters are directly associated with changes in the initial water/cement ratio of the composite.

2.6. Variation in the water absorption and length dimensions of the fibre–cement composites

After 28 days of cure, the composites were dried at 105 °C during 24 h in order to obtain their initial mass and length. Then, their water absorption capacity and their length changes were evaluated after their immersion into water for different times. These two parameters were measured within an interval of time of 28 h maximum, in order to avoid the interference of cement hydration and the matrix densification due to the possible reactions with water. The water absorption, WA (%), and the variation in length, LV (%), as a function of immersion times were calculated (Eqs. (3) and (4), respectively) and the effect of the fibre modification was deduced.

$$\text{WA}\ (\%) = \frac{(W_t - W_0)}{W_0} \times 100 \tag{3}$$

where W_0 and W_t are the weight of composites before and after immersion into water during t hours respectively.

$$\text{LV}\ (\%) = \frac{(L_t - L_0)}{L_0} \times 100 \quad (4)$$

where L_0 and L_t are the length of composites before and after immersion into water during t hours respectively.

2.7. Mechanical characterisation of the composites

Mechanical tests were performed after 28 days of cure, 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), modulus of rupture (MOR) and specific energy (SE) of the specimens, as described elsewhere [35]. The composites were tested wet after immersion for 24 h in water in order to normalise for the humidity condition.

3. Results and discussion

3.1. Characterisation of the fibre modification

XPS spectroscopy was used to characterise the cellulosic substrates investigated in this work, before and after treatment, as shown in Fig. 1a–d and Table 3. The full XPS spectrum of virgin (untreated) fibres shows that, before treatment, their surface is mainly constituted of carbon (signal at 284 eV) and oxygen atoms (signal at 532 eV) (Fig. 1a). After treatment, new peaks have appeared, namely: at around 102, 150 eV, attributed to Si2s, Si2p fingerprints, for MPTS- and APTS-treated samples, as presented in Fig. 1b and c respectively, and at around 399 eV, corresponding to nitrogen (N1s) for APTS- and AI-treated samples, as shown in Fig. 1c and d respectively.

In theory, pure cellulose exhibits O/C ratio of 0.83, as deduced from the theoretical formula [36]. This ratio was found to be 0.77 and 0.8 for the virgin pulps before and after extraction respectively (Table 3). The slight increase of O/C ratio results from the removal of some oxygen poor molecules, such as extractives and lignin fragments, as previously reported elsewhere [36–39]. The O/C ratio was found to be 0.75, 0.67 and 0.63 for the investigated fibres after treatments with MPTS, APTS and AI molecules respectively (Table 3). The decrease of the O/C ratio can be rationalised by the fact that the O/C ratios associated to all the grafting agents used here are lower than that of original material (lignocellulosic). Further evidences about the occurrence of the grafting are provided by the Si/C and N/C ratios. The first ratio shifted from 0 to 0.25 and 0.35, for MPTS- and APTS-grafted fibres respectively, whereas the second one varied from 0.01 to about 0.04 and 0.03 for APTS- and AI-treated fibres respectively. These data are in agreement with those reported in the literature for other lignocellulosics [15,16,39]. It is also worth to mention that for AI-treated samples, the N/C ratio varied very modestly (i.e., between 0.01 and 0.04) because of the low ratio between isocyanate functions and CH_2 units belonging to the long aliphatic chain (one nitrogen against 18 carbon atoms). Then, the C1s was deconvoluted, in order to quantify the relative abundance of carbon atoms types (Table 3). In theory, the pure cellulose exhibits two peaks in its deconvoluted C1s XPS spectra [37–39], namely: (i) C—O at 286.7 eV and associated to alcohols and ether groups. This peak is noted as C2 and corresponds to five carbon atoms (C_2—C_6 in Fig. 2), and (ii) O—C—O at 288.3 attributed to acetal moieties. This signal is noted as C3 (in XPS labelling data) and it corresponds to one carbon atom (C_1 of glucosidic moiety shown in Fig. 2).

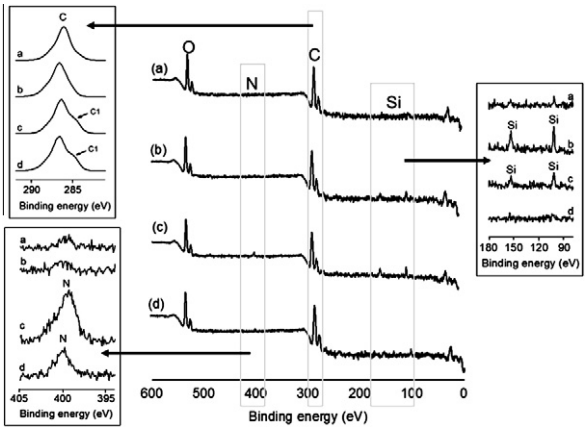


Fig. 1. Full XPS spectra of: (a) untreated (virgin); (b) MPTS-treated; (c) APTS-treated; and (d) AI-treated pulp.

The XPS analysis of pristine materials reveals the presence of four signals (C1, C2, C3 and C4). Thus, C1s peaks at 285.0, 286.7, 288.3 and 289.0 eV, attributed to C1 (C—H), C2 (C—O) and C3 (O—C—O and/or C=O) respectively, were detected. Here also theoretically speaking, two unexpected peaks: C1 and C4 were present. On a one hand, C1 signal corresponds to non-oxidised alkane-type carbon atoms and was already reported for other similar materials [36,37,39–41]. It was attributed to the impurities associated with the presence of residual lignin, extractive substances and fatty acids. On the other hand, C4 peak can be assigned to carboxylic functions originating from glucoronic acids borne by hemicelluloses, present at the surface of wood fibres.

The extraction of the fibres using the same conditions as those carried out for grafting reduces substantially the amount of C4 signals (from 3.1% to 1.2%), because such moieties are linked to easy removable compounds such as hemicelluloses. The C1s data of the APTS- and AI-treated fibres (Table 3) revealed a major difference related to the C1 peak (arrows in the detail of Fig. 1c and d), compared to that of virgin samples. In fact, the intensity of C1 increased from about 10% to ca. 22% (Table 3), as expected from the chemical structure of APTS and AI, which contains aliphatic sequence (especially AI grafting molecule). The intensity of C4 peak also increased for both MPTS- and AI-treated substrates, as expected from the molecular structure of MPTS (it contains a C4 moiety, i.e., O—C=O) and from the reaction of isocyanate with cellulose (urethane function, N—C(O)=O—). In fact, the intensity of C4 peak shifted from 1.2% to 3.1% and 3.2%, for MPTS and AI respectively. Finally, as, expected, the amount of C—N signal was also detected in the case of APTS and AI-treated samples. All the above mentioned facts give a clear evidence of the occurrence of the expected surface chemical modification of cellulose fibres.

Fig. 3 presents the average values of the dispersive and polar components of surface energy of the fibres, before and after treatment. Soxhlet extracted fibres present the highest surface energy as consequence of the fibre's surface purification (extraction of residual lignin and other constituents). This value is similar to that reported in the literature for similar fibres [27,42–45]. With the exception of APTS-treated fibres, the other treatments (MPTS and AI) decreased the surface energy of the fibres as a consequence of lowering its polar contribution. Such a finding proves the grafting occurrence and explains the decrease of the hydrophilic character of the resulting fibres. Similar results were found by Gaiolas et al. [27] for eucalyptus kraft fibres treated with MPTS under plasma discharges. The polar component of the APTS-treated fibres did not change significantly in relation to the extracted fibres, which shows that these fibres were not hydrophobized. The polar component value for AI-treated fibres agree with the best results for fibre hydrophobization reported in the literature [25,42,46].

The water retention values of the pulps confirm the hydrophobic character of the MPTS- and AI-treated fibres, and show that the

Table 3
XPS analysis of pulp samples, before and after modification with different coupling agents.

Fibres	O/C	Si/C	N/C	C1 C—C/C—H 284.9 eV	C1′ C—N 285.5 eV	C2 C—O 286.6 eV	C3 C=O 287.8 eV	C4 O—C=O 289.1 eV
Untreated (virgin)	0.77	–	0.02	11.7	–	66.7	18.7	3.1
Untreated (extracted)	0.80	–	0.01	09.8	–	68.3	20.7	1.2
MPTS-treated	0.75	0.25	0.02	15.9	–	64.7	18.7	3.1
APTS-treated	0.67	0.35	0.04	21.9	5.5	54.9	16.5	1.3
AI-treated	0.63	–	0.03	21.9	5.2	52.3	15.7	3.2

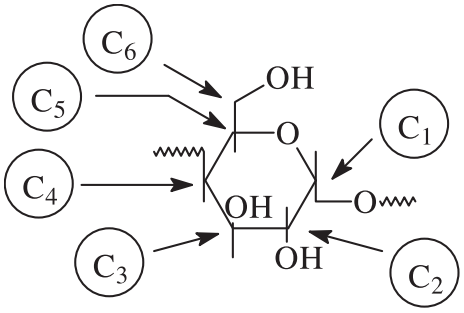


Fig. 2. The assignment of carbon atoms in glucosidic units.

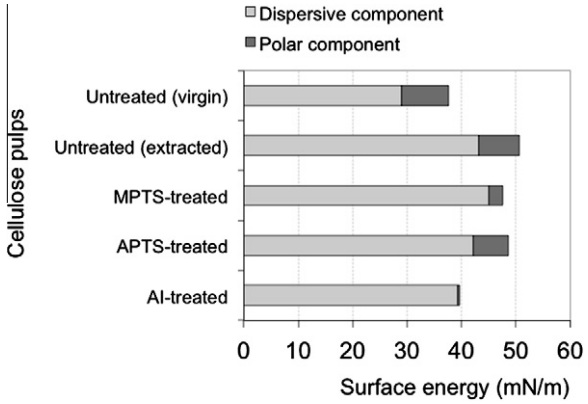


Fig. 3. Surface energy components (polar and dispersive) of the untreated and treated cellulose sheet fibres.

APTS treatment improved the hydrophilic character of the fibres (Fig. 4a). These data corroborate to those obtained by contact angle measurement, even though one could expect a more significant lowering of the water retention values associated to AI-treated fibres.

Fig. 4b presents the evolution of the fibre strength for the investigated fibres and shows a slight decrease in this parameter for all the treated samples, probably due to the further lignin extraction from the fibre cell wall during the fibre treatment process in solvent medium. The purpose is to modify the fibres surface without affecting their bulk properties and their physical integrity, which is expected from the use of soft experimental conditions that avoid the use of swelling and hydrolysing solvents. Fig. 4b also shows the slight decrease of fibre bonding index for MPTS-treated fibres as a consequence of their hydrophobized surface that decreased fibre bonding ability, while the increased fibre bonding index for APTS-treated fibres is a sign of their higher hydrogen bonding aptitude.

Fibre dispersion has been shown to significantly impact the fibre–cement processing [47] and the mechanical performance [48]; hence, it is important to emphasize that in spite of hydrophobic character of the AI- and the MPTS-treated fibres, it was possible to disperse them into water during the manufacturing process of the fibre–cement and no phase separation or de-lamination phenomena were observed.

In general, similar results are expected for fibre modification of bleached cellulose pulps from other vegetable resources. Fibre surface composition is limiting for effectiveness of the treatment. Bleached fibres are almost free from non-carbohydrates constituents of the fibres, such as wood extractives (surfactant-type molecules) and residual lignin, and therefore presents more hydroxyls available on their surface, and consequently higher are the number of sites for chemical coupling with APTS, MPTS and AI.

3.2. Effect of fibre treatment on processing of the fibre–cement composites

The fibre surface modifications led to changes in the fibre–cement processing. Fig. 5a depicts the lower water retention, after drainage for the composites made with MPTS- and AI-treated

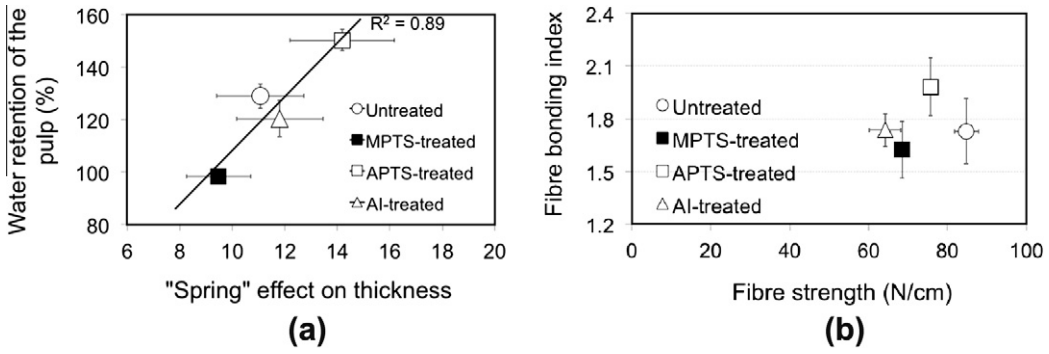


Fig. 4. Average values and standard deviation of: (a) water retention value (WRV) of the pulp in function of the "spring" effect on thickness of the composites; and (b) fibre bonding index in function of strength of the untreated and treated cellulose pulps.

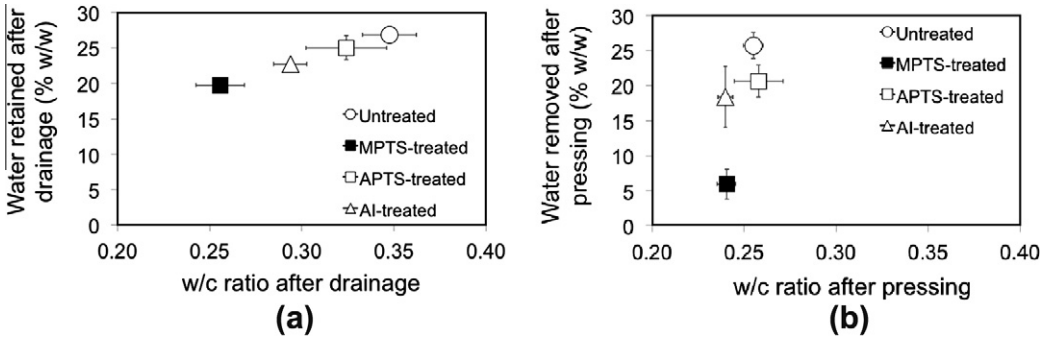


Fig. 5. Average values and standard deviation of: (a) water retained after drainage vs. water/cement (w/c) ratio after drainage; and (b) water removed after pressing vs. water/cement (w/c) ratio after pressing.

fibres, as a consequence of their lower hydrophilic character. This feature is also observed when examining the water/cement (w/c) ratio, before (Fig. 5a) and after pressing (Fig. 5b). Therefore it is expected that these composites would display high mechanical properties due to the lower w/c ratio [49]. On the contrary, the higher w/c ratio after pressing for the composites reinforced with untreated and APTS-treated fibre would predict materials with lower strength and durability [50,51].

The MPTS-treated fibres also presented a lower spring effect (Fig. 4a) due to the less hydrophilic fibres that decreased the fibre volume changes and consequently less changes on the thickness of the green sheets under and after pressing during the manufacturing. This is important because the water uptake and release by the fibres under negative and positive pressure, respectively, is the main responsible mechanism of the alkaline ions (resulting from the cement hydration) flow carrier into the fibres. Such phenomena cause the so called fibre mineralisation [35,52–55] and implies in its durability. Moreover, these features can lead to important interfacial damages between fibres and matrix, thus causing losses in the quality of the fibre bridging after curing. APTS-treated fibres led to higher spring effect after pressing (Fig. 4a), owing to the higher capacity of these fibres to retain and release water, as already shown by the other techniques. Good linear correlation ($R^2 = 0.89$) was observed between the water retention of the pulps and the "spring" effect of the green composites (Fig. 4a).

A good optimisation of the solids retention and drainage is crucial in the industrial process because of its effect on de-watering and green sheet formation (e.g. elephant skin appearance and delamination) and, as a consequence, on the overall efficiency of the machine [56]. Thus, according to the present results, MPTS-treated fibres could be considered as the most suitable reinforcing elements for cement formation structures in the case when high fibre loadings are needed (e.g. in the range of 10–15% weight by weight, or 17–25% by volume of solids). Coutts [57] and Coutts et al. [58] studied short (wood and non-wood) fibre effect and noticed that composites needed high fibre loadings (12–14% w/w) to reach their maximum strength. Nevertheless, high fibre loadings handicap the de-watering process and should be expected to turn more pronounced the elephant-skin appearance drawback. Therefore, in this case, less hydrophilic fibres should be considered as serious candidates to improve fibre–cement formation, mainly when the machine speed is the bottleneck. The problems of sheet formation in the fibre–cement industry can also be controlled through the proper flocculants selection, but, presently, its optimisation is considered as a competitive key issue for this industry [59,60].

Less hydrophilic fibres should also improve fibre–cement durability because fibres are less degraded by re-precipitation of cement hydration products inside their lumens [35]. The same advantages are expected to occur for extruding products probably with some benefits regarding the lower w/c ratio of the mixtures and the denser fibre to cement interface obtained by extrusion.

3.3. Water absorption and dimensional changes of the fibre–cement composites

Fig. 6 shows the effect of the fibre treatments on the water absorption and on the stability of the length dimension of the fibre–cement composites immersed in water during different times. APTS- and AI-treated fibres increased the water absorption (Fig. 6a) and the length variation (Fig. 6b) of the composites, while MPTS-treated fibres slightly decreased the water uptake and improved dimensional stability of the corresponding fibre–cement composites. The lower water retention value (Fig. 4a) of the MPTS-treated fibres corroborates with these findings and shows that this microstructure modification was effective to provide macro-structural changes in the fibre–cement composites. As presented in Fig. 3, the modification of the pulp with MPTS decreased the polar component of the surface energy. MPTS reacts with cellulose fibres by the formation of Si—O—C bonds [42]. Then, the methacrylic ends borne by MPTS are oriented toward the water–fibre interface, thus making the fibre surface much more hydrophobic. Instead, in the case of APTS- treated fibres, the increase of water absorption and length variation are associated to the presence of amine groups at the fibre surfaces, which increases the possibility of hydrogen bonds with water. Similar results were established for a diaminofunctional silane, as reported elsewhere [23,35]. The effect of AI-treated fibres is not as good as expected. In fact, in this case, the polar component is so low that any interaction and wettability with the cement components is strongly handicapped.

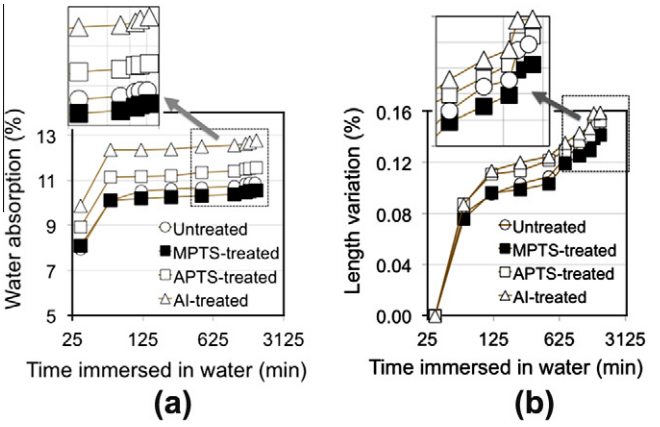


Fig. 6. (a) Water absorption and (b) length variation of the cement based composites in function of the time of immersion in water.

Such feature could create some defects and cracks in which more water can penetrate into fill the voids left by the non-wetted fibres in the cement composites. Moreover it may be expected that even if water contact angle is high at short period of time (e.g. after some minutes), these modified fibres can absorb water and modify their dimension after a long time (e.g. after some hours) immersed in water. This is confirmed by the difference between the beginning and the end of the curves in Fig. 6a and b. So, although the lower polar component for the AI-treated fibres, they were unsuccessful to reduce long term water uptake and dimensional stability of the fibre–cement composites.

3.4. Mechanical performance of the fibre–cement composites

Table 4 depicts the summary of the mechanical properties achieved with composites reinforced with untreated and treated pulps. LOP and MOR values do not seem to be influenced by the fibre treatment, while MOE values increased with APTS- and AI-treated fibres due probably to the improvement of fibre to cement adherence. If fibres adhere more to the cement, the incidence of pulled-out fibres is drastically reduced in a more packed structure in the composites [61]. Then, fibre rupture may occur and the fibre–cement composites absorb less energy from fibre to cement friction [2]. For this reason, APTS-treated fibres decreased the values of SE of the fibre–cement composites in relation to the other formulation (Table 4). Furthermore, the higher w/c ratio after processing for the composites with APTS-treated fibre would predict materials with lower strength and durability [50,51].

Instead, for AI-treated fibres it occurred the optimal situation, which was achieved by less hydrophilic surface (would be the protection of the cellulose fibres from water uptake), and without losing the quality of the fibre bridging that is responsible for the composite ductility. In the case of AI-treated fibres, the lower w/c ratio after processing (Fig. 5) and the isocyanate functions belonging to the long aliphatic chain in the fibre to cement boundaries seems to provide to the fibres the capacity to dissipate higher energy through the mechanism of pull out. Consequently, composites reinforced with AI-treated fibres had higher values of SE (Table 4).

MPTS-treated fibres guaranteed the pseudo-plastic behaviour of the composites at the age of 28 days, however MPTS-treated fibres have not promoted any significant impact on mechanical performance of the fibre–cement composites in relation to untreated fibres. The fact that MPTS-treated fibres present lower surface energy, water retention value and improved the dimensional stability of the composites is an indication of the potential of this fibre modification in minimising the degradation and embrittlement of the fibres during curing and weathering.

4. Conclusion

The surface modification of the unrefined eucalyptus fibres carried out in this work showed significant influence on the processing of the fibre–cement, water absorption, dimensional stability and mechanical properties of the composites. Results obtained with XPS-analyses and contact angle measurements indicated differences between the hydrophilic APTS-treated fibres and the less hydrophilic MPTS- and AI-treated fibres. The effects of these different grafting agents have been observed in the water retention values and on the fibre bonding indexes of the pulps. MPTS- and AI-treated fibres presented lower water retention values, while APTS increased the water retention value of the pulps and improved their capacity of hydrogen bonding. These observations point out that surface modification of the fibres with MPTS and AI is a promising approach to decrease the final water/cement ratio of the composites and serious candidates to improve fibre–cement formation, mainly when the machine speed is the bottleneck. The MPTS-treated fibres also decreased the spring effect during processing, which may reduce the mechanism of the alkaline ions flow carrier into the fibres. In comparison with virgin-fibre reinforced composites, MPTS-treated fibres decreased the water absorption of the fibre–cement composites and improved its dimensional stability, while the contrary occurred with APTS-modified fibres. LOP and MOR values do not seem to be influenced by the fibre treatment, while MOE values increased with APTS- and AI-treated fibres. The long aliphatic chain on the surface of the AI-treated fibres contributed to higher values of specific energy (SE), whereas the lower SE value for APTS-treated fibres is an indication of the improvement of fibre to cement adherence with this more hydrophilic fibre. MPTS-treated fibres have not promoted any significant impact on mechanical performance after 28 days of cure of the fibre–cement composites. These results contribute to ongoing research on fibre modification strategies that aim to improve the processing of fibre–cement products and their stability under weathering conditions.

Table 4
Average and standard deviation values of mechanical properties of composites reinforced with untreated and treated cellulose pulps.

Composites	LOP (MPa)	MOR (MPa)	MOE (GPa)	SE (kJ/m^2)
Untreated (extracted)	8.0 ± 1.7	12.7 ± 2.0	15.9 ± 1.3	2.5 ± 0.8
APTS-treated	8.8 ± 0.4	13.1 ± 1.1	18.5 ± 0.7	1.7 ± 0.4
MPTS-treated	9.3 ± 1.4	14.2 ± 1.0	16.7 ± 1.2	2.2 ± 0.2
AI-treated	8.5 ± 1.6	13.2 ± 1.4	20.5 ± 1.8	3.0 ± 1.0

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