EFFECTS OF *EUCALYPTUS* PULP REFINING ON THE PERFORMANCE AND DURABILITY OF FIBRE–CEMENT COMPOSITES

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TONOLI GHD, SANTOS SF, TEIXEIRA RS, PEREIRA-DA-SILVA MA, ROCCO LAHR FA, PESCATORI SILVA FH & SAVASTANO JR H. 2013. Effects of *Eucalyptus* pulp refining on the performance and durability of fibre–cement composites. Although *Eucalyptus* pulp has been widely used in the paper industry, there is limited information concerning its use as reinforcement in fibre–cement composites. The objective of this study was to evaluate effects of mechanical treatment (refining) of the *Eucalyptus* pulp on fibre properties as well as performance and microstructure of fibre–cement composites. The composites were evaluated before and after accelerated ageing cycles. The refining increased the capacity of *Eucalyptus* fibres to capture mineral particles, improving the adherence of the fibres with the matrix. This improved fibre–matrix interface led to better mechanical properties at 28 days of cure but higher mineralisation of fibres and consequently increased brittleness of composites after accelerated ageing (soak and dry) cycles. Unrefined fibres maintained the toughness of composites after ageing cycles. This indicates that refining may weaken the fibres thus affecting the mechanical performance (mainly decreasing modulus of rupture and toughness) of composites after ageing cycles. These results are useful for understanding effects of refined fibre conditions (morphology, mechanical strength and surface properties) on mechanisms of fibre–matrix adherence, fibre mineralisation and degradation of fibre–cement composites.

Keywords: Cellulose fibres, cement-based composites, microstructure, surface properties

TONOLI GHD, SANTOS SF, TEIXEIRA RS, PEREIRA-DA-SILVA MA, ROCCO LAHR FA, PESCATORI SILVA FH & SAVASTANO JR H. 2013. Kesan penghalusan pulpa *Eucalyptus* terhadap prestasi dan ketahanan komposit gentian–simen. Walaupun pulpa *Eucalyptus* digunakan dengan meluas dalam industri kertas, maklumat tentang penggunaannya sebagai penguat dalam komposit gentian–simen masih terhad. Tujuan kajian ini adalah untuk menilai kesan rawatan pulpa *Eucalyptus* secara mekanik iaitu penghalusan terhadap ciri gentian serta prestasi dan mikrostruktur komposit gentian–simen. Komposit diuji sebelum dan selepas kitaran penuaan dipercepat. Penghalusan meningkatkan kemampuan gentian *Eucalyptus* memerangkap zarah mineral dan seterusnya menambah baik lekatan gentian kepada matriks. Perhubungan gentian–matriks yang bertambah baik menghasilkan ciri mekanik yang lebih baik 28 hari selepas rawatan. Namun kadar pemineralan gentian menjadi lebih tinggi dan mengakibatkan peningkatan kerapuhan komposit selepas kitaran penuaan dipercepat (basah dan kering). Gentian yang tidak melalui penghalusan mengekalkan keliatan komposit selepas kitaran penuaan. Ini menunjukkan yang penghalusan mungkin melemahkan gentian dan seterusnya mempengaruhi prestasi mekanik (khususnya menurunkan nilai modulus kepecahan dan keliatan) komposit selepas kitaran penuaan. Keputusan ini berguna untuk memahami kesan keadaan gentian yang melalui penghalusan (morfologi, kekuatan mekanik dan ciri permukaan) terhadap mekanisme lekatan gentian–matriks, pemineralan gentian dan pendegradan komposit gentian–simen.

INTRODUCTION

Lignocellulosic materials and kraft pulp fibres have being increasingly used as reinforcement in cement-based materials in low cost construction in most developing countries (Adefisan 2011, Marzuki et al. 2011, Mendes et al. 2011, Tonoli et al. 2011a). Among kraft pulps, bleached *Eucalyptus* kraft pulp is the most abundant and has become increasingly more available. However, the potential of short fibre wood such as *Eucalyptus* species for the production of fibre–cement products deserves more examination. In tropical regions, *Eucalyptus* is a fast-growing hardwood species with good fibre qualities and relatively cheap market price.

The bond between cellulose fibre and Portland cement is due to mechanical interlocking or chemical (mainly hydrogen bonds) nature or a combination of both. Some studies suggest that the mechanical interlocking (or anchorage) between cellulose fibre surface and cement hydration products plays a significant role in bonding formation among these phases (Bentur 2000, Savastano Jr et al. 2005). The chemical composition of virgin pulp fibres (cellulose, polyoses, lignins and extractives) and cement hydration products developed on the fibre surface also exerts critical influence on the fibre to cement adherence (Tonoli et al. 2010a) and consequently on the mechanical performance of the ensuing composite (Savastano Jr & Agopyan 1999, Mohr et al. 2005). The cement dissolution/reprecipitation process during ageing makes the fibre/cement transition zone denser, approximating the surfaces of these particle phases, i.e. fibres and hydrated cement in the composite, which increase the bond strength by confined water (Rossetto et al. 2008, Rossetto et al. 2009). Subsequently, this also influences mechanical interlocking and chemical bonds between cellulose fibre and cement matrix.

One of the possible treatments to enhance physical bonds among fibre and cement matrix and consequently the mechanical performance of composites reinforced with cellulosic pulp is the refining process (Tonoli et al. 2011b). It is carried out in the presence of water, usually by passing the suspension of pulp fibres through a disk refiner composed by a relatively narrow gap between the rotor and the stator. Cellulosic fibres are intrinsically strong and refining greatly improves their malleability, which is necessary if the composite is manufactured using the Hatschek production method (Coutts 2005). The main effect of refining in cellulosic fibre structure as a result of mechanical action is the fibrillation of the fibres. These fibrillated fibres are responsible for the development of a net inside the composite mixture with the consequent retention of the cement matrix particles during the dewatering stage of the manufacturing process. The chemical moieties (OH reactive groups, for example) further generated on the fibre surface after refining may also be responsible for chemical bonds, mainly hydrogen bonding with the cement particles.

Pine fibres are usually highly refined in order to improve malleability, fibrillate their surface and improve fibre to cement bonding, processing and strength of the fibre–cement composites produced by the Hatschek process (Coutts 2005). However, there is no evidence that refining improves the durability of products reinforced with *Eucalyptus* pulp. Avoiding or decreasing the extent of fibre refining could be advantageous during stock preparation in the industry due to savings in refining energy as well as minimising damages caused in fibre cell wall, which, in general, decrease strength. Therefore, short cellulose fibres may improve the processing of the fibre–cement product with minimal costs in preparation.

Effects of *Eucalyptus* pulp refining on the chemical nature and morphology of the fibre surface, fibre strength, and microstructure and performance of fibre–cement produced by vacuum-dewatering and pressing have not been systematically examined. This would lead to better understanding of the mechanisms that affect the performance and degradation of cellulose fibre–cement materials produced via slurry dewatering.

The present work showed the progress in the engineering of cement-based composites made from tropical hardwood short fibre pulp. The main objectives of the present work were to evaluate the properties of unrefined and refined *Eucalyptus* pulp fibres and their effects on the microstructure, physical and mechanical properties, and durability of the fibre–cement composites.

MATERIALS AND METHODS

Materials

Commercial bleached and unbleached *Eucalyptus urograndis* kraft pulps were used. Pulp was refined in a disc refiner as reported in Tonoli et al. (2011b). Discs were 300 mm diameter with 3 mm width bar, 3 mm width groove and 7.5° angle bar configuration, resulting in approximately 1.5 km/rev cutting edge length for the double disc refiner. Pulp was passed several times through the refiner until the achievement of different refining levels associated with the Canadian standard freeness (CSF) values. The CSF test is a widely accepted standard measure of the drainage properties of pulp suspensions and it relates well to the initial drainage rate of the wet pulp pad during the dewatering process. Low freeness values (less than 300 mL) are indicative of high extent of fibrillation and/or shortage of fibres, leading to long drainage periods during the test. CSF values were determined after each refining level following TAPPI T 227 om-99 (TAPPI 1999) standard.

High ordinary strength Portland cement (OPC) Type III according to ASTM C150 (ASTM 2009) and ground carbonate material were used as the matrix of the fibre–cement composite. Ground carbonate material (commonly used in agriculture) was used as partial substitution for OPC in order to reduce cost. Oxide compositions of the OPC and the ground carbonate material were accomplished by X-ray fluorescence spectrometry. Oxide composition of the OPC was (percentage by mass) 19.4% SiO_2, 63.5% CaO, 4.1% Al_2O_3, 2.3% Fe_2O_3, 3.1% MgO, 1.1% K_2O, 3.0% SO_3 and 0.2% Na_2O. Oxide composition of the ground carbonate material was (percentage by mass) 9.0% SiO_2, 39.1% CaO, 2.2% Al_2O_3, 1.2% Fe_2O_3, 8.9% MgO, 0.2% P_2O_5, 0.4% K_2O, 0.1% TiO_2, 0.1% MnO and 0.1% Na_2O. According to particle size distribution by laser granulometry 2.19, 50% of the particles were smaller than 11.0 and 16.2 µm for OPC and ground carbonate material respectively. Most particles (90%) were smaller than 27.3 and 64.4 µm for OPC and ground carbonate material respectively.

Pulp characterisation

The main morphological properties of the fibres were analysed by Pulptec™ MFA-500. This equipment comprises basically a charge-coupled device camera that captures images of the fibre/water suspension and records them for further analysis with software that carries out measurements and statistical corrections (Wätzig 2008). The images were crowded with fines and fibres. The software distinguished between fibres and fines through size criteria (length and width). A fine element was considered as any detected object present in the pulp with dimensions lower than those of fibres, i.e. length under 200 µm or width under 5 µm (Tonoli et al. 2009a). Microfibrils were attached to the fibre and expressed as percentage in length of microfibrils. Broken ends were detected as fibres having fibrils at their ends.

Kappa number of the pulps was determined following the standard SCAN C 1:77 (SCAN 1977). The total residual lignin content (TRLC) was calculated according to TRLC = kappa number/6.546 as described by Laine et al. (1994). The water retention value (WRV) of the pulp is an experimental measurement of the capacity of the fibres to retain water. It was performed according to TAPPI UM 256 (TAPPI 1981) standard. The fibre strength and fibre bonding index were measured with a zero-span tester according to the standard methods of TAPPI T 273 cm-95 (TAPPI 1995) and T 231 pm-96 (TAPPI 1996) respectively.

Fibres were viewed in a field emission scanning electron microscope at 2 kV. Multimode Nanoscope IIIa atomic force microscope digital instrument at tapping mode (TM-AFM) was used to evaluate the fibre surface morphology before and after refining, by means of height and phase imaging data acquired simultaneously. Silicon cantilever with spring constant of around 70 N m^{-1} and scan area of 3 µm × 3 µm was used and all images were obtained in atmospheric (air) environment (temperature around 25 °C and relative humidity between 50 and 65%). The higher areas of the fibres were preferred for these measurements, as previously detailed by Tonoli et al. (2010b). The raw data images were processed and reconstituted using the software NanoScope® III.

Production of composites and accelerated ageing

Cement-based composites were reinforced with unbleached *Eucalyptus* kraft pulps. Optimal fibre–cement formulation was chosen based on

previous studies (Tonoli et al. 2009a, Tonoli et al. 2012). Suspensions with approximately 20% solids were prepared using the following constituents (percentage by dry mass): 10.0% of cellulose pulp, 77.2% of OPC, 12.8% of ground carbonate material and distilled water. The corresponding percentage by dry volume of the cellulose pulp was around 18%. The cement-based composites (flat pads) measuring 200 mm × 200 mm and around 6 mm thick were produced at laboratory scale using slurry vacuum dewatering process followed by pressing (Tonoli et al. 2009b). The final water/cement ratio achieved after this process was around 0.3. The fibre–cement pads were immediately wet sealed in a plastic bag to the initial cure at room temperature for 2 days and then immersed in lime-saturated water for 26 days. Pads were cut wet into four 165 mm × 40 mm flexural test specimens using a water-cooled diamond saw. Specimen thickness was approximately 5 mm.

On completion of the immersion curing, some of the specimens were tested at 28 days after production and some were successively subjected to soak and dry cycles as described in Joaquim et al. (2009) based on the EN 494 (EN 1994) standard. Each soak and dry cycle had a total period of 6 hours corresponding to 2 hours 50 min of immersion in water at around 25 °C, followed by an interval of 10 min (air exposition at room temperature) and then 2 hours 50 min of heated air at around 70 °C with a final interval of 10 min. Each cycle was routinely repeated 200 times in an equipment performing accelerated ageing test.

Characterisation of the fibre–cement composites

Mechanical tests were performed using the testing machine equipped with 1 kN load cell. Four-point bending configuration was employed to evaluate the limit of proportionality (LOP), modulus of rupture (MOR), modulus of elasticity (MOE) and toughness of the specimens (Tonoli et al. 2009b). The deflection values were divided by the major span (135 mm) of the bending test and called specific deflection (ε). The composites were tested wet after 24 hours of immersing in water in order to normalise the humidity condition. Six specimens were used for testing of each design. Physical properties, namely, apparent porosity (AP) and bulk density (BD) values were obtained from the average of six specimens for testing of each design following the ASTM C 948–81 (ASTM 1981) standard.

Scanning electron microscopy equipped with back-scattered electron detector was applied to cut and polished surfaces for characterisation of fibre to matrix interface. Cementitious phases were recognised by the contrast of atomic number of different chemical elements using the back-scattered electron mode. Dark and light areas were related to lower and higher atomic numbers respectively. Energy-dispersive X-ray spectrometry atomic mapping was also performed in order to localise the carbon, calcium and silicon atoms on the same polished surface specimens. The preparation of specimens for back-scattered electron analyses was accomplished with low pressure (25 kPa gauge) impregnation using epoxy resin. Back-scattered electron samples were ground with silicon carbide grinding paper with sequential grit sizes of 120, 320 and 500 for 4 min each using ethanol as lubricant. A final polishing was carried out using, in turn, 8–4, 4–2 and 1–0 μm diamond polishing compound for 6 min per size. Polished samples were carbon coated and examined under a microscope.

RESULTS AND DISCUSSION

Effect of pulp refining on fibre properties

Table 1 shows that fibre shortening produces small particles (shorter than 200 μm). They are commonly called fines, which also contain band-like materials from both primary and secondary wall layers of the fibres (Somboon et al. 2007). The refining level CSF 250 mL increased fines content and the average width of *Eucalyptus* fibres. The increase of fibre width by outer cell wall swelling and internal fibrillation after refining (Fardim & Durán 2003) should lead to an increase of fibre volume (Tonoli et al. 2009a).

One of the effects of refining on cellulosic fibre structure is the fibrillation of the fibre surface (Coutts 2005). Both microfibrils and broken ends increase the surface area of fibres, which made them more reactive with cement particles. As shown in Table 1, fibrillation increased with refining. This contributes to the development of a net inside the composite (Tonoli et al. 2009a).

Figure 1a presents the individual fibre strength and fibre bonding index (fibre bonding capacity) assessed by zero-span measurements of the pulps

at different refining rates. *Eucalyptus* unrefined was the strongest fibre. Refining decreased individual fibre strength. This is a negative aspect with regard to the reinforcement capacity of the fibre. However, refining increased the hydrogen bonding capacity of fibres and consequently the strength of the fibre network. The objective of the present work was not to achieve optimum *Eucalyptus* refining conditions for reinforcement of the cement matrix. It is reasonable to state that the best refining level should be a balance between fibre strength and fibre adhesion.

The increase in water retention value (Figure 1b) in refined fibres indicates an improvement of their hydrophilic character due to cleaning of fibre surface from non-carbohydrates constituents of fibres (Belgacem et al. 1995) such as wood extractives (surfactant-type molecules) and residual lignin. Refining was reported to change the chemical composition of fibre surface (Fardim & Durán 2003). The authors indicated that an enrichment of the fibre surface with cellulose and xylan took place as well as a decrease of lignin content after refining. This is demonstrated in Figure 2, as the higher the refining level (lower CSF value), the lower the total residual lignin content in the pulp. Lignin and neutral components were reported to dissolve from the fibre surface or covered by carbohydrates after refining (Fardim & Durán 2003). Therefore, it is expected that in refined pulps, the number of free OH groups in the fibre surface is higher than that of unrefined pulps as cellulose contains 3 OH reactive groups for each six carbons, while lignin presents 1–2 free OH groups for each 10 carbons in its chemical structure (Kajanto & Niskanen 1998). Consequently, refining favours the fibre–water interaction and thereby increases the hydrophilic character of fibre. This explains why unrefined *Eucalyptus* pulp present lower water retention value (Figure 1b) compared with refined pulp. The higher affinity of refined fibres to water is a remarkable surface property ensuring improvement in fibre to matrix adherence. It is, however, a disadvantage with regard to preservation of fibre from chemical degradation as alkaline pore water is the main agent of fibre weakening within the cementitious matrix (Tolêdo Filho et al. 2003, Claramunt et al. 2011).

Figure 3 explains what happens in the fibre cell wall with refining. The microfibrils measured around 30 nm in diameter for both refined and unrefined fibres. The microfibrils of refined fibre (Figure 3b) were more exposed than microfibrils in unrefined fibre (Figure 3a). This is a consequence of the mechanical treatment promoted in the fibre surface during refining. The refining energy is sufficient to partially rupture the bonds between microfibrils, leading

Table 1 Morphological properties of the unrefined and the refined *Eucalyptus* fibres used in the composites

Pulp	CSF (mL)	Average length (mm)	Average width (μm)	Rate of microfibril (%)	Broken ends (%)	Fines content (%)
Unrefined	665	0.82 ± 0.04	15.6 ± 0.1	0.36 ± 0.04	12.0 ± 0.4	22.4 ± 0.6
Refined	250	0.76 ± 0.05	17.3 ± 0.1	0.68 ± 0.01	18.3 ± 0.3	35.0 ± 0.2

Fines content = particles shorter than 200 μm; CSF = Canadian standard freeness

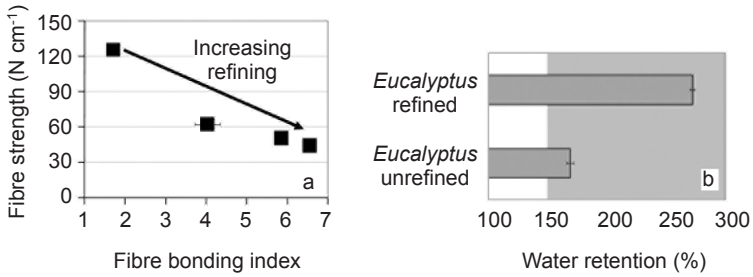

Figure 1 Average values and standard deviations of (a) fibre strength in relation to fibre bonding index at different refining rates and (b) water retention values of unbleached refined and unrefined *Eucalyptus* fibres

to a more opened fibre cell wall. This also explains the higher water retention presented in Figure 1b. In fibre–cement composites, the higher the fibrillar surface of fibres, the higher their capacity to bond with cement matrix (Coutts 2005).

Effect of pulp refining on fibre-cement performance and microstructure

Table 2 presents the mechanical and physical properties of the composites reinforced with unbleached unrefined (CSF 665 mL) and refined (CSF 250 mL) *Eucalyptus* pulp. Refining significantly increased the MOR (Figure 4) and LOP (Figure 5a) of composites after 28 days of cure due to the increase in fibre fibrillation and the consequent improvement of fibre adherence to cement matrix. Toughness (Figure 4) and MOE (Figure 5b) of the composites after 28 days of cure were not influenced by refining.

Pulp refining decreased significantly the apparent porosity (Figure 5a) and increased significantly the bulk density (Figure 5b) of the composites after 28 days of cure (Table 2). This result was also reported by Tonoli et al. (2011b)

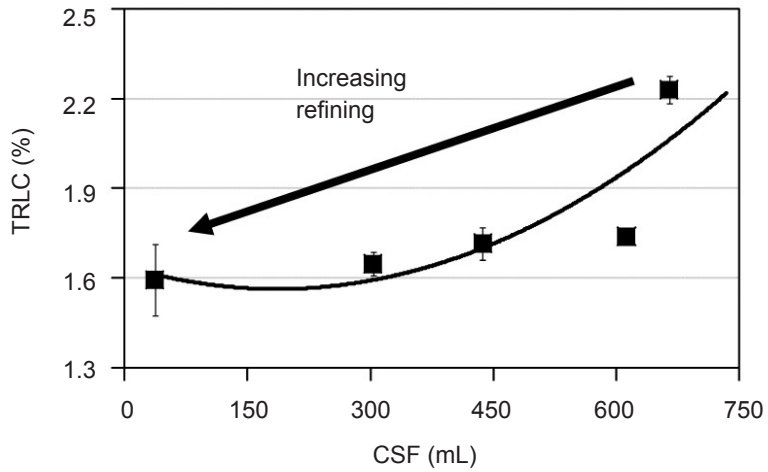

Figure 2 Average values and standard deviations of the total residual lignin content (TRLC) at different refining levels (CSF) of the unbleached *Eucalyptus* pulp

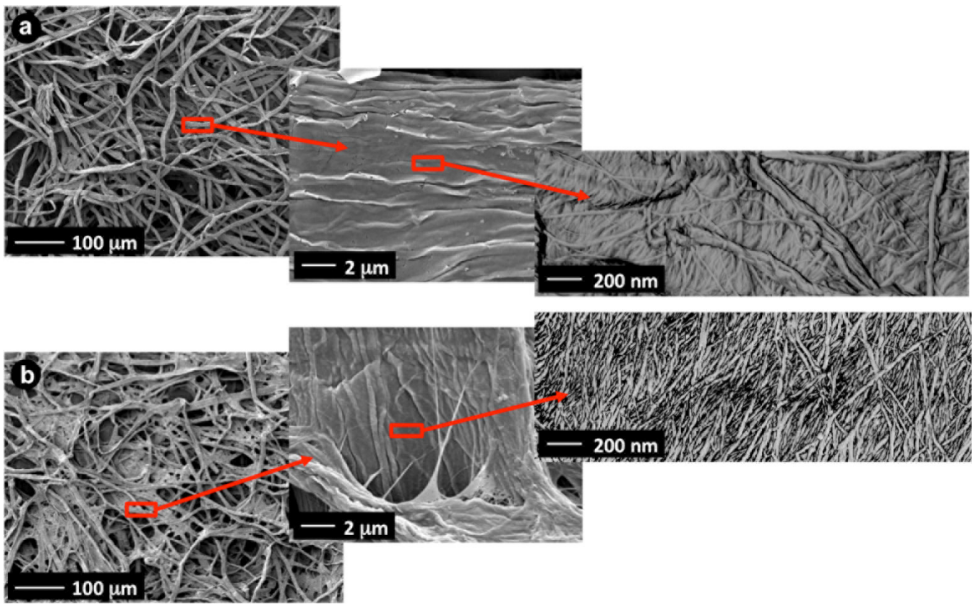

Figure 3 Typical scanning electron micrographs (left and centre) and atomic force microscope images (right) of (a) unrefined (CSF 600 mL) and (b) refined (CSF 130 mL) *Eucalyptus* bleached fibres

in sisal refined pulp. This could be attributed to the improvement of the fibre malleability and the fibrillation generated by refining, which improved the packing of the matrix particles into the composite.

The MOR of composites with unrefined pulp increased significantly after 200 accelerated ageing cycles (Figure 4) due to a decrease of pores at the fibre–matrix interface (Figure 6b) as a consequence of the reprecipitation of cement hydration products into those pores (Tonoli et al. 2010c). The LOP and MOE of composites with unrefined and refined pulps also increased significantly after ageing cycles (Figure 5). However, the decrease of the mechanical strength (Figure 1a) of individual fibres with the present refining level decreased the toughness of the composite after 200 ageing cycles (Figure 4). The reprecipitation of high alkaline pore water within the fibre to cement interface and inside the fibre lumen can induce the stiffening of cellulose fibres by means of mineralisation (Tolêdo Filho et al. 2000, Mohr et al. 2005).

The toughness of composites with refined pulp decreased drastically after ageing is also due to the progressive improvement of the fibre to matrix adherence provided by the reprecipitation of cement hydration products in the fibre–matrix interface (Figure 6a). The typical ruptures of the fibre cell wall (arrows 1) due to the high level of pulp refining are depicted in Figure 6a. These damages caused by the present refining level permitted the reprecipitation of cement hydration products into fibres (mineralisation) that decreased their flexibility and increased their mineralisation. Refining leads to internal fibrillation or delamination (disjointing of the cell wall layers) that allows the reprecipitation of cement hydration products between the fibre cell walls (arrow 2 in Figure 6a), decreasing fibre flexibility and increasing fibre mineralisation. Nevertheless, the existence of voids or pores around the refined fibres was not observed, which increases fibre to matrix adherence. This improvement in adherence is associated to better

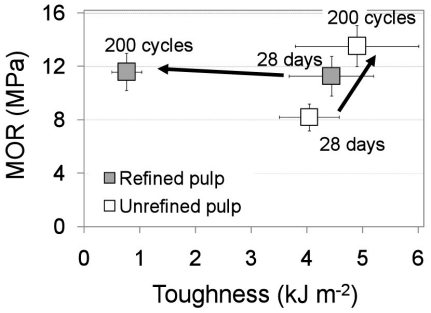

Figure 4 Average values and standard deviations of MOR (modulus of rupture) vs toughness of the composites reinforced with unbleached unrefined (CSF 665 mL) and refined (CSF 250 mL) pulps after 28 days of cure and 200 accelerated ageing cycles; arrows indicate the behaviour of properties after ageing cycles

Table 2 Mean and standard deviation values of mechanical and physical properties of composites reinforced with unbleached unrefined (CSF 665 mL) and refined (CSF 250 mL) *Eucalyptus* pulp

Property	Composite			
	Unrefined pulp		Refined pulp	
	28 days	200 cycles	28 days	200 cycles
LOP (MPa)	4.0 ± 0.8 Bb	6.4 ± 0.7 Fa	6.9 ± 1.2 Af	9.4 ± 0.5 Ee
MOR (MPa)	8.2 ± 1.0 Bb	13.5 ± 1.5 Ea	11.3 ± 1.5 Ae	11.6 ± 1.4 Fe
MOE (GPa)	6.5 ± 0.8 Ab	11.5 ± 1.7 Fa	7.1 ± 1.1 Af	13.7 ± 0.4 Ee
TE (kJ m^{-2})	4.0 ± 0.5 Aa	4.9 ± 1.1 Ea	4.4 ± 0.8 Ae	0.7 ± 0.3 Ff
AP (%)	37.3 ± 1.0 Aa	35.7 ± 1.3 Eb	35.8 ± 0.8 Be	33.4 ± 1.8 Ff
BD (g cm^{-3})	1.44 ± 0.04 Bb	1.58 ± 0.04 Ea	1.51 ± 0.02 Ae	1.49 ± 0.06 Fe

LOP = limit of proportionality, MOR = modulus of rupture, MOE = modulus of elasticity, TE = toughness, AP = apparent porosity, BD = bulk density; different letters indicate significant differences between composites in Tukey test at 5% significance level, capital letters (A vs B or E vs F) in the same row represent comparisons between composites with unrefined and refined pulp, small letters (a vs b or e vs f) in the same row represent comparisons between composites at different ageing conditions (28 days vs 200 cycles)

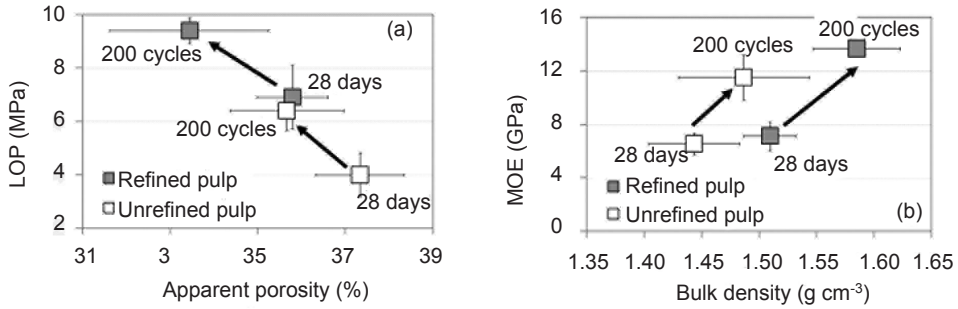

Figure 5 Average values and standard deviations of (a) limit of proportionality (LOP) vs apparent porosity and (b) modulus of elasticity (MOE) vs bulk density of the fibre–cement composites reinforced with unbleached unrefined (CSF 665 mL) and refined (CSF 250 mL) *Eucalyptus* pulp; composites were tested after 28 days of cure and 200 accelerated ageing cycles; arrows indicate the behaviour of properties after ageing cycles

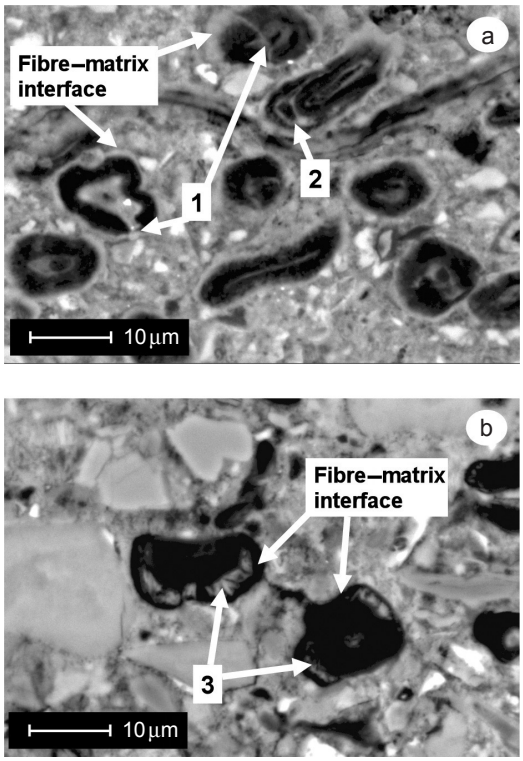

Figure 6 Typical back-scattered electron images of cut and polished cross-section surfaces of composites after 200 ageing cycles reinforced with (a) refined (CSF 250 mL) and (b) unrefined (CSF 665 mL) *Eucalyptus* pulp; arrows 1 are examples of the rupture of the fibre cell wall, arrow 2 is an example of the cement reprecipitation between the cell wall layers of the fibre, arrows 3 show the cement reprecipitation around fibres (fibre–matrix interface)

packing of particles and higher densification of composite (Tonoli et al. 2007). Improvement in adherence is also due to greater occurrence of hydrogen bonding caused by a decrease of capillaries among phases (Rossetto et al. 2008, Rossetto et al. 2009).

In composites with unrefined fibres, reprecipitation of cement hydration products after 200 cycles occurred only around the fibres (arrows 3 in Figure 6b), i.e. into the pores at the fibre–matrix interface. In this case, there were still pores at the interface (arrows in Figure 6b), but most of the fibres were free from cement products in their lumens. The lower fibre mineralisation and the fact that unbleached unrefined fibres present higher initial mechanical strength (Figure 1a) are explanations for higher toughness values of composites after 200 ageing cycles (Figure 4).

These observations on the dissolution/reprecipitation of cement hydration products around the fibres in their lumens and matrix pores (Tonoli et al. 2010c) also explain the decrease of the apparent porosity values (Figure 5a) and the increase of the bulk density values (Figure 5b) of the composites after the 200 cycles (Table 2).

In the energy dispersive X-ray spectrometry atomic mapping of the calcium atoms of polished surfaces corresponding to refined fibre-reinforced composites, calcium (green) was located within the fibre cell wall (Figure 7d). The concentration of carbon (red) decreased in the fibre cell wall of refined fibres. In composites reinforced with unrefined fibres, the carbon atoms were still present in great amount within the fibre cell wall (Figure 7c). Thus, the components and morphology of fibre cell wall in unrefined *Eucalyptus* fibres seem to play an important role in minimising mineralisation and degradation of fibres during weathering.

CONCLUSIONS

Mechanical treatment (refining) of the *Eucalyptus* pulp improved the fibre to matrix interface, improving the microstructure of the composite (apparent porosity and packing of the matrix particles) and the initial mechanical performance (after 28 days of cure) due to the higher physical anchorage and hydrogen bonding. Nevertheless, the present refining conditions (CSF 250 mL) led to higher degradation of fibres in the cement matrix due to fibre cutting and damages caused in the fibre cell walls. Refined fibres presented accelerated mineralisation into the composites and unrefined fibres presented higher performance (higher MOR and toughness) after 200 ageing cycles. Despite cellulose pulps being highly refined for the manufacture of the fibre–cement in the industry, the morphological properties of the *Eucalyptus* pulp (shorter fibres and higher number of fibres per gram) can improve fibre network even with low refining extent.

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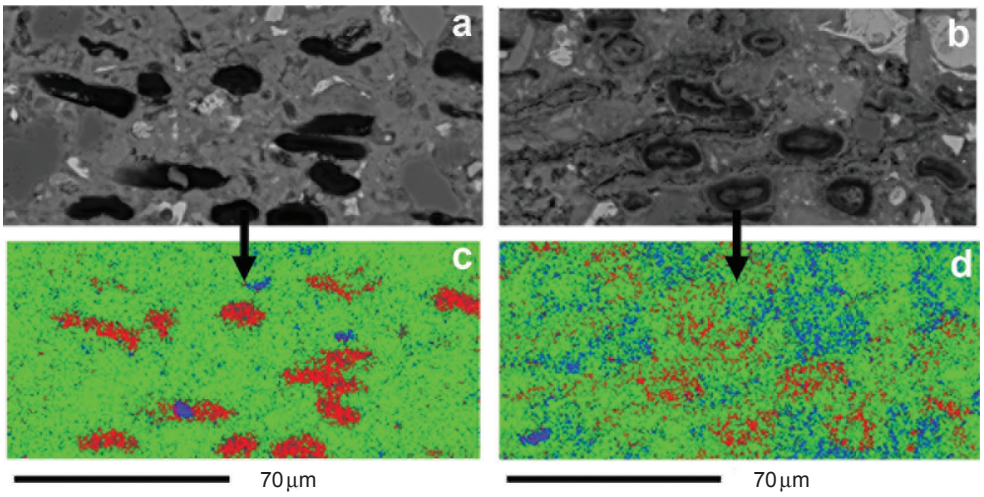

Figure 7 Typical back-scattered electron images (above) and EDS atomic mapping (below) of C (red), Ca (green) and Si (blue) of the polished cross section surfaces of composites reinforced with: (a and c) unrefined (CSF 665 mL) and (b and d) refined (CSF 250 mL) *Eucalyptus* fibres images obtained after 200 ageing cycles

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