# EFFECTS OF EUCALYPTUS FIBRE SURFACE PROPERTIES ON THE MICROSTRUCTURE OF CEMENT BASED COMPOSITES

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## ABSTRACT

The objective of the present work is to evaluate the effects of the surface properties of the unrefined eucalyptus pulp fibres on their performance in cement based composites. Unbleached pulp presents a thin layer on the fibre surface that is rich in lignin, hemicellulose and extractives. Such a layer acts as a physical and chemical barrier to the cement attack and consequently reduces its penetration into the fibres' cell wall. The lower polar contribution to the surface energy of the unbleached fibres suggests that these fibres are less hydrophilic than their bleached counterpart. Atomic force microscopy (AFM) reveals the changes that occur on the fibre surface after pulp bleaching and contributes to understand the quality of the resulting fibre-cement interface. Pulp bleaching improved the fibre/cement interfacial bonding, while fibres in the unbleached pulp were less susceptible to the re-precipitation of cement hydration products into the fibre cavities (lumens). Therefore, unbleached fibres can improve the long term performance of the fibre-cement composite due to their delayed mineralization.

## KEYWORDS:

Atomic force microscopy; Cellulose fibre; Cement; Contact angle; Fibre-cement; Surface energy; Eucalyptus pulp.

## INTRODUCTION

Kraft pulp fibre-reinforced cement-based materials have being increasingly used in most developing countries as construction materials (Ikai et al., 2010; Tonoli et al., 2010a; Tonoli et al., 2010b). The bond between cellulose fibre and cement is of physical (mechanical interlocking) or chemical nature (mainly hydrogen bonds), or a combination of both (Coutts, 1988). Some previous studies suggested that the mechanical interlocking (or anchorage) between cellulose fibre surface and cement hydration products, plays a significant role in bonding formation among these phases (Coutts and Kightly, 1984; Bentur, 2000; Savastano Jr. et al., 2003; Savastano Jr. et al., 2005). The chemical composition of the virgin pulp fibres

(cellulose, polyoses, lignins and extractives) and that of cement hydration products developed on the fibre surface also exerts critical influence on the fibre to cement adherence, and consequently on the mechanical performance of the ensuing composite (Savastano Jr. and Agopyan, 1999, Mohr et al., 2005; Tonoli et al., 2009a; Joaquim et al., 2009).

On the other hand, the highly alkaline pore water within the fibre/cement interface can induce the stiffening of the cellulose fibres by means of the mineralization phenomenon proposed elsewhere (Bentur and Akers, 1989; Tolêdo Filho et al., 2000; Wei et al., 2004; Mohr et al., 2006), which leads to significant losses in the mechanical performance of the full composites. Hence, the optimal situation would be to protect the cellulose fibres from water uptake using less hydrophilic surfaces (naturally or after an adequate treatment), but maintaining the quality of the fibre bridging that guarantees composite ductility. Although some studies reported this as problematic, there is still a lack of relevant information about the chemistry and morphology of the cellulose fibre surface so as to understand the main mechanisms influencing the performance and the degradation of cellulose fibre-cement materials. The objective of the present work is to investigate the effect of the surface properties of unrefined eucalyptus kraft fibres on their performance and mineralization phenomenon in the cement-based composites.

## EXPERIMENTAL

### Materials

Conventional unrefined unbleached and bleached eucalyptus kraft pulps were investigated. The bleaching sequence consisted of oxygen (O), acid extraction (A), ozone (Z), chlorine dioxide (D), and hydrogen peroxide (P) stages. Kappa number was measured according to SCAN C 1:77 (1977) standard. Calculation of the total residual lignin content was determined by: TRLC = (kappa number) / 6.546, as described by Laine et al. (1994). Determination of pulp and wood extractives was according to Tappi T 204 cm-97 (1997) standard. The mean viscosity of the pulps was determined in cupriethylendiamine diluted solution (SCAN CM 15:99, 1999).

### Surface morphology by atomic force microscopy (AFM)

Atomic force microscope (AFM): Multimode Nanoscope IIIa Digital Instument was used in tapping-mode (TM-AFM). The instrument permits the collection of height and the phase imaging data simultaneously. The spring constant of the silicon cantilever was around 70 N $m^{-1}$ (Digital Instruments, 1996); the scan area was: 3 x 3 $\mu m^2$; all measurements were performed in atmospheric (air) environment. Images were collected from around 10 different fibres for each sample so that the main axis of the fibre was parallel to the slow scan axis of the AFM, with an accuracy of some degrees (~$10^o$).

### Contact angle (CA) and surface energy of fibres

Cellulose hand sheets were prepared according to Tappi T 205 sp-95 (1995) standard using the Pulmac ASF-C1 facility. Instrument for preparation of cellulose hand sheets:. The measurement of CA and the surface energy was performed with a dynamic contact angle absorption tester (DataPhysics OCA) equipped with a charge-coupled device (CCD) camera collecting up to 200 images $s^{-1}$. The main characteristics of the liquids applied in this work for CA measurements were presented in Tonoli et al. (2009). The dispersive and polar components of the surface energy of the cellulose pulp samples were determined according to the approach of Owens and Wendt (1969).

### Fibre strength and bonding properties of the cellulose pulps

The fibre 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 (1995) and T 231 pm-96 (1996).

### Composite preparation and accelerated ageing

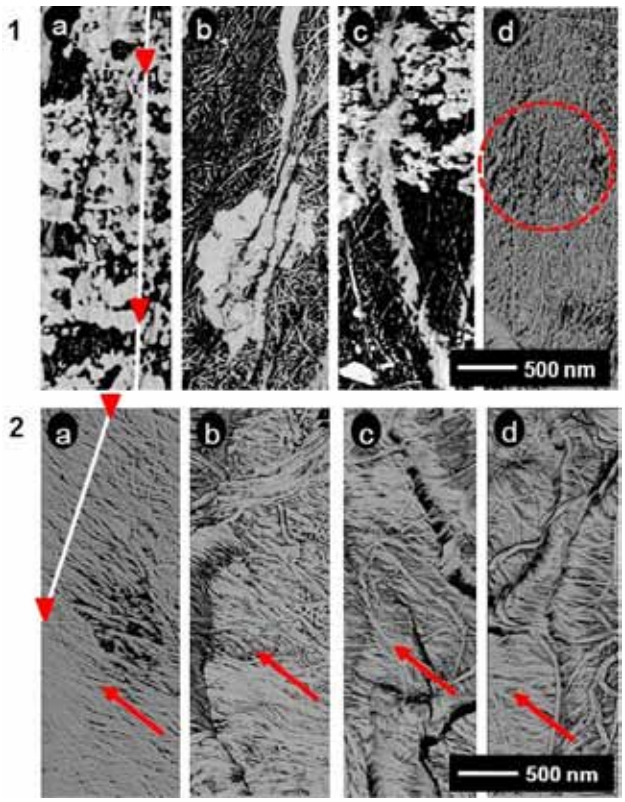
The cement based composites were molded in plates measuring 200 mm x 200 mm. Preparation in a laboratory scale device using slurry vacuum de-watering followed by pressing technique, as described in details by Tonoli et al. (2010b). The fibre-cement formulation was based on previous studies (Tonoli et al., 2007; Tonoli et al. 2009)with 5.0% pulp, 77.2% OPC (ordinary Portland cement) CPV-ARI (NBR 5733, 1983), and 17.8% ground carbonate material.

On completion of the water immersion curing, composites were successively subjected to soak and dry cycles as described in details by Tonoli et al. (2009) based on the EN 494 (1994) standard. Each soak and dry cycle was repeated 200 times, performing the accelerated ageing test.

### Microstructural characterization of the fibre-cement composites

Scanning electron microscopy (SEM): A back-scattered electron (BSE) detector was used for the observation of cut and polished surfaces. The BSE imaging permits the easy identification of cementitious phases by the contrast of the atomic number of the different elements. Dark and light-grey areas are related to lower and higher atomic numbers respectively. Identification of the chemical composition in different spots was done by energy dispersive spectrometry (EDS). The preparation of specimens for BSE and EDS analyses was accomplished as described in Tonoli et al. (2009).

The mercury intrusion porosimetry (MIP) technique was adopted to evaluate the pore size distribution as usually applied in the characterization of cement-based materials (Tonoli et al., 2010b).




**Figures 1 and 2 – Typical AFM images of unbleached (1) and bleached (2) eucalyptus fibres. Line and red arrows in (a) show one point of the roughness measurements. Circle depicts a granular region. Red arrows indicated the approximate microfibril orientation in relation to the main axis of the fibre.**

## RESULTS AND DISCUSSION

### Surface morphology of the pulp fibres

Unbleached pulp presented higher total residual lignin content (TRLC) and higher wood extractives amount. Bleaching led to viscosity loss, which is caused by the carbohydrate depolymerization resulting from hydrolysis of the glycosidic bonds (Torres et al., 2005). AFM shows that the surface of the unbleached eucalyptus fibres have a thin smooth layer in the majority of the samples (Figure 1), interpreted as being middle lamella rich in lignin and extractives. Gustafsson et al. (2003) also explained the amorphous non-carbohydrates on the fibre surface of slash pinus as being lignin and extractives. In some cases, little granular structures occur (circle in Figure 1d) and were interpreted as extractives precipitated on the primary cell wall (Böras and Gatenhom, 1999; Osterberg et al., 2006). Similar results were reported by Koljonen et al. (2003) for pulps with high contents of lignin and extractives. However, these authors stated that lignin can also be present in a non-granular shape on the fibre surface.

Johansson (2002) has studied mechanical pulp fibres and has showed that the extractives may, in some cases, form monomolecular films, which may, at least partially, cover the fibre surface, whereas lignin on the surface of the cellulose fibrils is mostly expected to appear in the form of patches, which are thicker than 10 nm. Laine et al. (1994) have applied electron spectroscopy for chemical analysis (ESCA) and found a lignin

layer with thickness of about 10 nm on the fibre surface. In the present work the lignin coating layer (Figures 1a-c) has a thickness between 10 and 20 nm and obscured the underlying microfibrils. According to Gustafsson et al. (2001), the nonfibrillar structures covering the surface of the microfibrils can equally be attributed to the components re-precipitated from the cooking liquor. The granular structures were identified as surface lignin or a mixture of lignin, hemicelluloses and extractives. This view is supported by the observation that the decrease of the relative amount of the granular phase correlates well with the decreasing kappa number value of the birch and pine samples under evaluation in the referred study (Simola et al., 2000).

Below the residual middle lamella and granular structures, misaligned microfibrils are observed in Figure 1. They are randomly oriented, typically from the primary layer of the fibres, as widely reported in the literature (Illston et al., 1979; Gram, 1988). These structures and misaligned microfibrils were not detected after the bleaching sequence, as shown in Figure 2, in which the AFM images reveal that the changes occurred in the fibre surface. In the bleached pulp, the typical surface structure was fibrilar (showing microfibrils) and oriented at around 40° with respect to the longitudinal fibre axis (arrows in Figure 2), confirming that it is referred to the inner wall layers of the fibre. Such a degree of orientation is typical for the S1 secondary wall layer (Gram, 1988).

**Surface energy of the pulp fibres**

The lower hydrophilic character of the unbleached cellulose fibres is indicated by the water contact angle of around 90°, compared to 40° for bleached cellulose fibres. Böras and Gatenholm (1999) also reported higher water contact angles on lignin-rich surfaces. Unbleached eucalyptus pulp presented higher contact angles with other polar liquids (glycerol and ethylene-glycol) when compared with bleached eucalyptus pulps, leading to lower surface energy. Bleaching of the pulps increased the surface energy of the fibres, due to the increments in the dispersive and polar components. The increase in the polar component in bleached fibres indicates an increase of their hydrophilic character due to the cleaning of the fibre surface from non-carbohydrates constituents of the fibres (Belgacem et al., 1995), as wood extractives (surfactant-type molecules) and residual lignin. According to Koljonen et al. (2003), the ozone bleaching used in the present research substantially modifies or removes the lignin from the surface. It is known that ozone reacts mainly with lignin, breaking the unsaturated bonds and producing carbonyl and carboxyl end structures and thereby increasing the hydrophilicity of the fibres (Katz and Scallan, 1983). In bleached pulps, the number of free OH groups on the surface is higher than that in the unbleached pulp because cellulose contains 3 OH/$C_6$, while lignin 1-2 free OH groups/$C_9$ (Kajanto and Niskanen, 1998). Based on this it is obvious that unbleached eucalyptus pulp displays lower surface energy, and negligible polar contribution when compared to bleached pulp fibres. The lower affinity of unbleached fibres to water may be helpful to avoid fibre degradation, as alkaline pore water is the main agent for fibre degradation in the cementitious matrix.

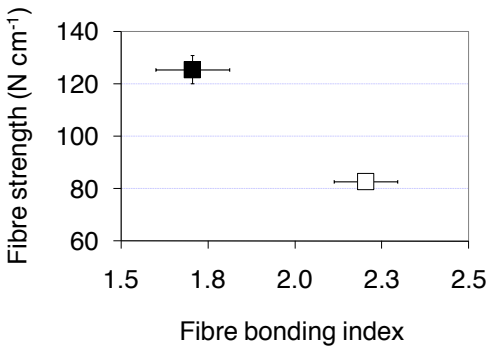



**Figure 3 – Average and standard deviation values of fibre strength in relation to fibre bonding index. Black and white squares are related to eucalyptus unbleached and bleached pulps respectively.**

**Effect of fibre surface properties on fibre strength and fibre bonding capacity**

Figure 3 presents the decrease of fibre strength (assessed by zero-span measurements) due to depolymerization reactions of cellulose chains during bleaching (Brown and Dawe, 1996). Despite the fibre strength loss with bleaching, the increased fibre bonding index is a sign of the improvement in hydrogen bonding between the bleached fibres. This assertion is supported by the contact angle measurements, where the surface free energy and the polar component of the bleached fibres are higher than in the unbleached fibres. Additionally, the peroxide bleaching stage, used in the present work, may have caused the softening

of the fibre cell walls, resulting in greater interfibre bond-forming capacity (Torres et al., 2005). The AFM images also show the higher fibrilar surface of the bleached fibres (Figure 2). In the fibre-cement composites, the higher the fibrillar surface of the fibres, the higher the capacity of the fibres to bond with cement matrix (Coutts, 2005).

**Effect of fibre surface properties on fibre-cement microstructure**

The SEM micrographs (BSE) of cut and polished fibre-cement sections after exposition to 200 accelerated ageing cycles are presented in Figure 4. In the composites with unbleached eucalyptus pulp (Figure 4a) the lumens are free from visible cement hydration products (spot 1). The opposite is true for the composites prepared with bleached fibres; the lumens are visibly filled by cement hydration products rich in Ca (Figure 4b), as proved by the spots 3 and 4. It is obvious that bleaching made the fibres more susceptible to mineralization, because extractives, lignin, hemicelluloses and pectins are removed, which act as a chemical and physical barrier to the penetration of Ca ions into the fibres. Mohr et al. (2006) also reported that lignin and wood extractives play a protecting role against fibre mineralization.

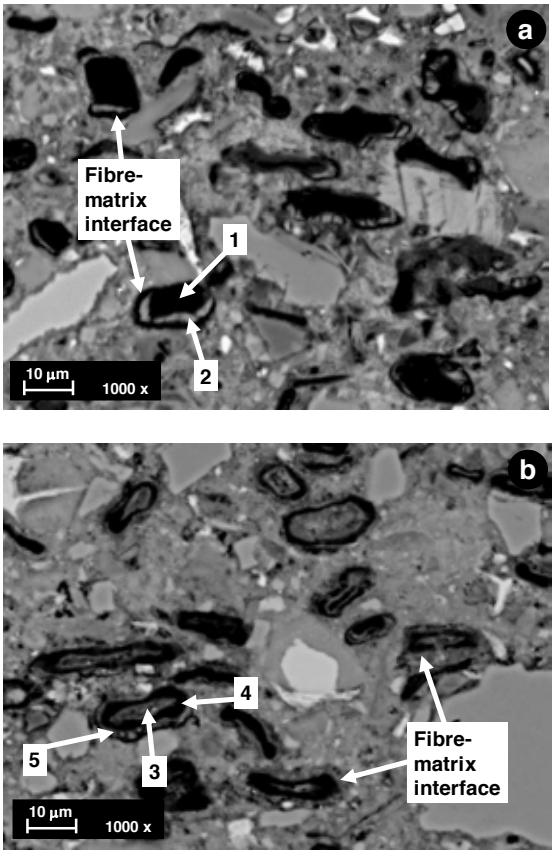



**Figure 4 – Typical SEM BSE images of composites reinforced with: (a) unbleached and (b) bleached eucalyptus pulp, after 200 accelerated ageing cycles. EDS spot analyses are signalized in the images (spots 1–5).**

For unbleached eucalyptus fibres, the cement hydration products re-precipitated around the fibres by the formation of sulphate-rich phase layers (e.g. ettringite and monosulphate), as evidenced by the spot 2 in Figure 4a. For bleached fibrous material, the re-precipitation is observed inside and around the fibres (spots 3 and 5, respectively, in Figure 4b).

The rougher more fibrillated surface, and the higher surface energy of the eucalyptus bleached fibres indicate the higher capacity of these fibres to bond with other phases. An improved interface between the bleached fibres and the cement matrix is observed in Figure 4b. This observation is corroborated by the results of MIP (Figure 5), as the amount of mercury intruded in pores below 1 µm was higher in composites reinforced with unbleached fibres. Pores below 1 µm occur mainly at the fibre to cement interface (arrows in Figure 4a).

The apparent higher adhesion of the bleached fibres with cement matrix can be interpreted as their being more resistant to be pulled out from the matrix. The adhesion of the fibres tends to be improved after ageing for both bleached and unbleached fibres, due to the re-precipitation of cement hydration products around the fibres, as presented in Figure 4. When fibres adhere more strongly to cement or are degraded by re-precipitation inside their lumens, fibre rupture occurs and the fibre-cement composites absorb less energy of fibre to cement friction, failing by brittle fracture after ageing (Savastano Jr. et al., 2003).

The fact that unbleached fibres present a smoother surface and lower surface energy is an indication that these fibres can be pulled out from the matrix more easily than their bleached counterpart, leading to composites with higher toughness (ductility) after ageing (Mohr et al., 2005). Furthermore, unbleached fibres in the composites were usually free from hydration products into their cavities (lumen), thus unbleached fibres remain more flexible and less brittle than their bleached homologues.

## CONCLUSIONS

Unbleached eucalyptus pulp fibre is surrounded by a thin lignin and extractives rich layer on its surface, which acts as a physical and chemical barrier to penetration of dissolved cement components into the fibres. The lower polar contribution to the surface energy of the unbleached fibres confirms that these fibres are less hydrophilic than their bleached counterparts. AFM and surface energy measurements demonstrate clearly the changes on the fibre surface due to bleaching. Bleaching roughens the fibres exposes the fibrils and makes them more permeable to liquids as a result of removing the amorphous lignin and extractives. Consequently, the interfacial bonding between bleached fibres and cement is improved. On the other hand, unbleached fibres are less susceptible to cement re-precipitation into the fibre cavities and therefore the mineralization in the fibre-cement composite is delayed. This is an indication that the unbleached fibres may contribute to composites with higher ductility after ageing by allowing great dissipation of energy through the mechanism of fibre pull-out.

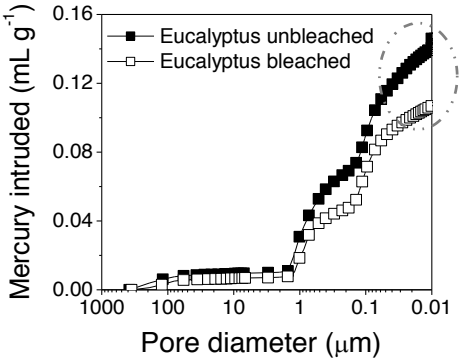



**Figure 5 – Cumulative mercury intrusion porosimetry (MIP) of the composites reinforced with unbleached and bleached eucalyptus pulps.**

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