ACCELERATED CARBONATION ON VEGETABLE FIBRE REINFORCED CIMENTITIOUS ROOFING TILES

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ABSTRACT

The main objective of the present work was to evaluate the effects of accelerated carbonation on mechanic performance and physical characteristics of vegetable fibre reinforced cimentitious roofing tiles. Fibre reinforced tiles with undulate shape were produced by slurry dewatering technique using ordinary Portland cement, carbonate filler and sisal (*Agave sisalana*) Kraft pulp. The pulp was mechanically refined and mixed with a cement matrix reaching slurry at 40% of solids prior to dewatering and pressing. Wet curing was provided up to 28 days of total age. Part of the tiles were then submitted to CO_2 rich environment during seven days and/or accelerated ageing of 100 soak & drying cycles. Maximum load and toughness were evaluated by three point bending configuration. Physical characteristics, such as water absorption, bulk density and apparent porosity, were determined according to ASTM C 948-81 Standard. The diffractometer and titration with potentiometric pH transducer were used to evaluate the efficiency of accelerated carbonation on tiles. The results showed that accelerated carbonation was efficient to transform hydroxides into carbonates. In consequence of this accelerated carbonation the maximum load and toughness have increased approximately 25% and 80% respectively. Besides water absorption and apparent porosity decreased with carbonation (~30 and 20%) while bulk density increased (~20%) as a clear indication of the densification of the composite. The apparent high permeability of capillary pores has permitted the fast diffusion of CO_2 inside the matrix and the formation of carbonates. The improvement of toughness suggests that the fibres retained their capacity of energy absorption in the fragile matrix. The results of the ongoing work indicate the utilization of accelerated carbonation in the production of cement based composites reinforced with vegetable fibres as an effective procedure to mitigate the degradation suffered by the cellulosic fibres in the less aggressive medium.

Keywords: Sisal pulp, cellulosic pulp, fibre-cement, ordinary Portland cement.

INTRODUCTION

Natural fibres as reinforcement of fragile matrices based on cimentitious materials have provoked great interest in developing countries based on their low cost, availability, economy of energy, and also as asbestos substitute regarding environmental concerns (MacVicar et al., 1999). According to Swamy (1980), the use of composites in flat sheets, roofing tiles and pre-manufactured components, can represent significant contribution for the infrastructure of these countries.

The available technologies for asbestos-free fibre-cement are well accepted in the developed world. However, they require large investments that are many times impracticable, considering the reality of the low income countries. The developing societies must look for alternative raw materials. Appropriate fibres and binders different of the traditional raw material, frequently involve higher costs and great consumption of energy in their processing (Coutts, 2005). Another concern is the durability of the alternative products, as well as their compatibility to the useful life of the components destined to buildings of low income population (Savastano Jr. et al., 1999).

Precedent studies (Agopyan et al., 2005; Devito, 2003) using compaction by vibration for production of roofing tiles reinforced with natural fibres observed losses of 50% in average to mechanical performance after one year of natural exposure. Authors attributed the decrease in the mechanical properties to the degradation of the vegetable fibres, which was accelerated by the alkaline media of the cement matrix, combined with the warm and humid climate of exposition. Beside, the bad dispersion of the unrefined cellulosic pulp disturbed the efficiency of the matrix reinforcement.

An alternative to increase the durability of the natural fibres in cement matrix is carbonation. The carbonation is the reaction of cement hydration products with carbon dioxide (CO_2) available in the air. Amongst the hydration products of the cement paste, the one which reacts more quickly is the $CaOH_2$, resulting in the $CaCO_3$ (Gram, 1988). This process starts in the most external layer of the composite and it moves gradually to the internal layers, through the fissures and the system of permeable pores. Tests involving artificial carbonation of products with asbestos fibres have shown the formation of around 35 - 40% of $CaCO_3$, with the consequent increase of composite strength, reduction of specific energy and water absorption (Jones, 1946). Tolêdo Filho et al. (2003) reported a significant increase in durability of the composite with 109 days of exposure to carbon dioxide atmosphere

The present study was carried out in an attempt to produce durable fibre-cement roofing tiles using conventional sisal (*Agave sisalana*) Kraft pulp by the slurry dewatering technique. The work also evaluated the effect of accelerated carbonation on physical and mechanical performance of vegetable fibre reinforced cimentitious tiles and its consequent durability after ageing.

EXPERIMENTAL

Fibre preparation

Conventional Kraft sisal pulp (up to 3% total Klason lignin) was provided by Lwarcel Celulose e Papel, Brazil. The unrefined pulp was submitted to a stirring process in water and was post-refined by several passes through 300 mm disc refiner until the achievement of CSF 220 mL refinement degree. The Canadian Standard Freeness test (CSF) is a widely recognized standard measure of the drainage properties of pulp suspensions (Coutts & Ridikas, 1982). It relates well to the initial drainage rate of the wet pulp pad during the de-watering process. Low freeness values (less than 300 mL) are indicative of high degrees of external fibrillation and/or shortage of the fibres, leading to long drainage periods during the test. The refinement greatly improves the manufacturing processes based on slurry dewatering techniques followed by pressing (Savastano Jr. et al., 2000).

The main physical attributes of the pulp presented in Table 1 were characterized by particle size analyzer Galai CIS-100. The analysis with Galai CIS-100 consists in the evaluation of the attributes of the whole fibrous material present in the refined pulp.

Table 1 – Pulp and fibre physical properties [a].

Pulp CSF (mL)	Average length (mm)	Average width (μm)	Aspect ratio	Coarseness (mg/100 m)	Fibrous material (10^6 fibres/g)	Fines content (%)
220	1.13 ± 0.05	18.7 ± 0.2	60	9.99 ± 0.61	8.9 ± 0.9	40.6 ± 1.3

(a) Pulp and Paper Laboratory, Department of Forestry Engineering of the Federal University of Viçosa, Brazil.

Production of the roofing tiles

Formulations used in the production of roofing tiles are described in Table 2 and were based on previous studies published elsewhere (Roma Jr., 2004).

Table 2 – Formulations used in the production of undulate roofing tiles.

Raw materials	Content (% by mass)
Refined sisal Kraft pulp (CSF 220mL)	4.7 [a]
Portland Cement (CP V-ARI) [b]	78.8
Ground carbonate material	16.5

(a) Equivalent to 4% by volume, (b) NBR 5733 (1983) (clinker + gypsum = 100 - 95% by mass; carbonate material = 0 - 5%).

Pulp was previously dispersed in water by mechanical stirring at 1,700 rpm during 30 min. The mixture was prepared with approximately 40% of solids, and stirred during additional by 20 min. The slurry was transferred to the storage container located in the upper part of the equipment shown in Figure 1. This container is moved by an automated system for the transference of the mixture to a chamber with approximate dimensions of 500 mm long, 275 mm wide and 8 mm thick. The dewatering system was applied during 30 s for the drainage of the excess water while the undulate tile was formed and pressed by pneumatic pistons. Afterwards, negative pressure was applied to the upper device for additional 30 s and the conformed tile was transferred from the molding chamber to the undulate mold conferring its final shape.

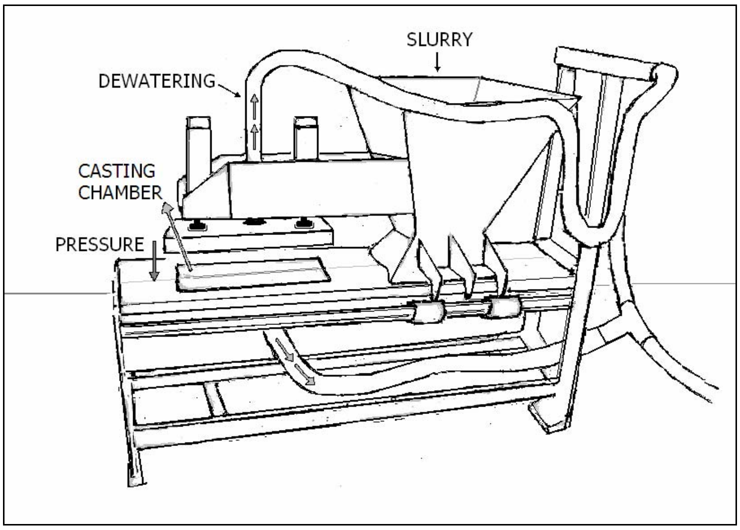

Figure 1 – Schematic view of the semi-automated device used for roofing tiles molding.

The initial cure was carried out in controlled environment (25 ± 2ºC, 70 ± 5% RH – relative humidity) when the roofing tiles remained in the molds protected with plastic bags for two days. After this period, the roofing tiles were removed from molds and submitted to immersion in water for the following 26 days.

After curing by the total period of 28 days, tiles were submitted to the physical and mechanical tests. The remaining series were destined to the soak & dry accelerated ageing tests, as well as accelerated carbonation. The roofing tiles were tested in saturated condition after at least 24 h of immersion in water.

Accelerated carbonation

Accelerated carbonation of the roofing tiles was carried out in a climatic chamber with carbon dioxide (CO_2)

saturated environment and with controlled temperature and humidity (20°C and 75% RH respectively). The roofing tiles were submitted to the climatic chamber environment during one week until the complete carbonation of the samples. The carbonation degree was evaluated by the exposure to a solution with 2% of phenolphthalein diluted in anhydrous ethanol as described by Silva (2002) and Agopyan et al. (2005).

Diffractometer and titration with potentiometric pH transducer

The phases of the samples were analyzed by X-ray diffraction in a Rigaku Rotoflex RU-200B equipment with horizontal goniometry, multipurpose camera and monochromator. The conditions of operations were defined as voltage of 50 kV, electric current equal to 100 mA, velocity of 1 degree/min and step of 0.02 degree. Samples used in this analysis were ground and passed through 325 mesh screen.

Titration with potenciometric pH transducer was used for the determination of carbonation rate instead of the consumption of calcium (or magnesium) hydroxide. The samples were assessed at 28 days of age and after 100 ageing cycles with or without the prior exposition to accelerated carbonation.

The titration analysis procedure combines the use of visual indication of phenolphthalein and potentiometric pH transducer (Harris, 2001; Mendham et al., 2002). In this procedure, 200 mg of the sample were dispersed in 40 mL of distilled water in combination with 5 drops of alcoholic solution with 2% of phenolphthalein as the visual indicator. Titration was performed with a standard solution of HCl 0.1 mol/L and a pH transducer equipment.

The first point of the indicator change of red to clear pink is related to pH value around 8. It corresponds to the volume of HCl necessary to neutralize the existing hydroxides in the suspension. After the first point of changing, the HCl standard solution continued to be added until pH value around 2 was reached. At this point, the mixture was submitted to boiling nitrogen for the consumption of all the carbonic acid generated. The excess of HCl was titrated with NaOH 0.1 mol/L standard solution in the presence of phenolphthalein, with pH value around 7.

The number of hydroxide moles, $n_{hydroxides}$, present in the sample was calculated in accordance with the Eq.(1):

$$n_{hydroxides} = \frac{V(1)_{HCl} \cdot C_{HCl}}{2000} \tag{1}$$

Where: $V(1)_{HCl}$ is the first gotten equivalence volume on titration, and C_{HCl} is the concentration of the HCL standard solution, in mol/L.

The total number of moles, or either, the sum of $n_{hydroxides}$ and $n_{carbonates}$, was calculated from the total volume added of HCl standard solution until pH was approximately 2, $V(2)_{HCl}$, as well as the concentration of this solution in mol/L, C_{HCl}, and the volume of NaOH standard solution, V_{NaOH}, with concentration in mol/L, C_{NaOH}, according to Eq.(2):

$$n_{total} = \frac{V(2)_{HCl} \cdot C_{HCl}}{2000} - \frac{V_{NaOH} \cdot C_{NaOH}}{2000} \tag{2}$$

Eq.(3) represents the calculation of the number of carbonate moles, $n_{carbonates}$, given by the difference between the total number of moles, n_{total}, and the number of hydroxide moles $n_{hydroxides}$, that is present in specific portion of the sample:

$$n_{carbonates} = n_{total} - n_{hydroxides} \quad (3)$$

Getting the number of carbonate moles, $n_{carbonates}$, and the number of hydroxide moles, $n_{hydroxides}$, present in the portion of analyzed sample, it was possible to calculate the percentage of each species in the sample of interest by Eq.(4) and Eq.(5):

$$\%\ hydroxides = \frac{n_{hydroxides}}{n_{total}} \cdot 100 \quad (4)$$

$$\%\ carbonates = \frac{n_{carbonates}}{n_{total}} \cdot 100 \quad (5)$$

Soak & dry accelerated ageing cycles

The soak & dry accelerated ageing cycles involved comparative analysis of the physical and mechanical performance of the tiles before and after this test. The roofing tiles were successively immersed in water at 20^{o}C ± 5^{o}C during 170 min, followed by interval of 10 min, and then exposed to the temperature of 70^{o}C ± 5^{o}C for 170 min in a ventilated oven and final interval of 10 min. This procedure was based on recommendations of the EN 494 (1994) Standards. Each soak & dry set represents one cycle and was performed for 100 times (i.e., 100 cycles).

Physical and mechanical characterization tests

Water absorption (WA), bulk density (BD) and apparent void volume (AVV) results were obtained from the average of twenty specimens for each formulation, following the procedures specified by ASTM C 948-81 (1981).

Mechanical tests were performed in a universal testing machine Emic DL-30,000 equipped with 5 kN load cell. A three-point bending configuration with undulate shape and following the procedures described by Gram & Gut (1994) was used in the determination of maximum load of rupture, ML, and toughness results, TE. Toughness (TE) was obtained by integration of the load-deflection curve to the point corresponding to a reduction in load carrying capacity to 60% of the maximum observed. A span of 350 mm and a deflection rate of 5 mm/min were adopted in the bending test. The deflection during the bending test was collected by the deflectometer positioned in the down side of the tile. Toughness was defined as the energy absorbed during the flexural test. The absorbed energy was calculated by integration of the area under the load–deflection curve.

Statistical analysis

The results of physical and mechanical tests were subjected to statistical analysis. It was carried out according to the Method of Minimum Squares and using the PROC GLM procedure of the Statistical Analysis System program, v. 9.1 (SAS, 1995). The thickness of the roofing tiles was a continuous variable that has influenced the dependent variables (properties of the roofing tiles). A design of hierarchical classification was used for the unbalanced data with the support of a co-variable (thickness of the tiles). The characteristics of the roofing tiles were described in accordance to the following hierarchical design (Eq.7), in order to determine the significance of observed differences amongst sample means at the 95% confidence level ($\alpha = 0.05$).

$$y_{rs} = \mu + E_r + b_1 \left(h_{rs} - \overline{h}\right) + e_{rs} \quad (7)$$

Where:
y_{rs} = observed average for the ageing r; μ = constant for all observations; E_r = fixed effect of ageing r, for r = 1 (noncarbonated and unaged), 2 (100 cycles) and 3 (carbonated + 100 cycles); b_1 = linear regression coefficient of y_{rs} characteristic in relation to thickness of the tiles; h_{rs} = thickness of the s tile, in mm, observed at ageing r; $\overline{h}$ = average thickness of the tiles; e_{rs} = random residuary effect associated with the observations at the ageing r, with average equal to zero and σ^2_e variance.

RESULTS AND DISCUSSION

Physical properties

The results and respective statistical analysis for the physical properties of the undulate roofing tiles are presented in Table 3. The WA, AVV and BD values of the roofing tiles for 28 days were similar to that found by Roma Jr. (2004) that evaluated the roofing tiles produced with ground blast furnace slag (GBFS), reinforced with 3% by mass of sisal pulp and processed by vibration. The following results were obtained for WA, AVV and BD respectively: 31.0%, 42.3% and 1.35 g/cm^3. Such figures are still in accordance with the limit of 37% recommended by the Brazilian standard (NBR 7581, 1993). On the other hand they can be considered worse than those found by Agopyan et al. (2005) that have reported WA values below 16%.

In general, ageing cycles have contributed for the reduction of the porosity of roofing tiles. However the accelerated carbonation followed by the 100 cycles (C-100c) was the treatment that most affected the physical properties of the roofing tiles. The reduction of the porosity provided by carbonation could be the responsible for the improvement of mechanical properties. Accelerated carbonation reduced around 20% the apparent void volume (AVV) of the tiles. The significant reduction of the water absorption and the densification of the carbonated roofing tiles indicated the effective adsorption of the carbon dioxide and the formation of new hydration products in the cement matrix. Silva (2002) also reported the reduction of approximately 15% of the porosity of cellulose fibre cement after its accelerated carbonation.

The water tightness test did not present formation of drops on the underside of the tiles after 24 h under 250 mm of water column pressure. The water damps were more evident for the non-aged tiles in comparison to those carbonated and/or subjected to 100 cycles (C-100c and 100c).

Mechanical properties

The results of the statistical analysis for the mechanical properties are presented in Table 3. Load-deflection curves of the roofing tiles are presented in the Figure 2. As observed in Table 3 the maximum load (ML) supported by the roofing tiles did not suffer a significant reduction after the ageing cycles. These results are considerably above the limit of 425 N recommended by Gram & Gut (1994) for 8 mm thick tiles.

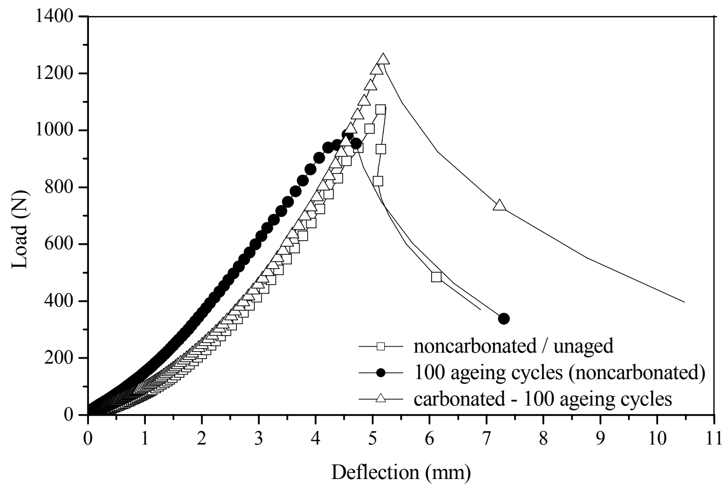

Figure 2 – Load-deflection curves for the tiles of the different treatments.

Ageing did not cause significant decrease in the maximum load (ML) and toughness (TE), in relation to the unaged tiles tested with 28 days. Moreover, the results of ML and TE (Table 3) were superior to those found in preceding works with roofing tiles produced by vibration. Savastano Jr. et al. (1999) obtained maximum load and toughness values around 550 N and 1.6 kN.mm respectively for roofing tiles reinforced with 2% by volume of unrefined macro-fibres and pulps (coconut, eucalyptus and sisal) at 28 days of age. It seems that the pulp refinement adopted in the present research contributed to the homogeneous distribution of fibres during the molding of the roofing tiles, with the consequent better anchorage of fibres in the matrix and improved strength of the product. Besides, the net of fibres was more efficient in the retention of the cement particles during the vacuum dewatering process, providing a suitable packing during the pressing stage and more effective fibre-matrix bonds.

Table 3 – Average values and standard deviations for water absorption (WA), apparent void volume (AVV), bulk density (BD), maximum load (ML) and toughness (TE) of the roofing tiles evaluated according to the different ageing treatments (r).*

r (ageing)	WA (%)	AVV (%)	BD (g/cm^3)	ML (N)	TE (kN.mm)
Noncarbonated / unaged	32.8 ± 1.1 A	44.2 ± 0.7 A	1.35 ± 0.03 B	1074 ± 244 B	3.4 ± 1.3 B
100c [1]	33.3 ± 0.9 A	44.0 ± 0.9 A	1.32 ± 0.01 B	1030 ± 345 B	3.5 ± 1.7 B
C-100c [2]	23.3 ± 0.7 B	35.8 ± 1.8 B	1.56 ± 0.01 A	1284 ± 221 A	5.9 ± 2.0 A

* Different letters indicate significant differences, which capital letters (A and B) in the same column represent comparisons between ageing. [1] 100c: 100 soak & dry cycles; [2] C-100c: carbonation followed by 100 soak & dry cycles.

Accelerated carbonation effect

The X-ray diffraction patterns in Figures 3 and 4 show the presence of calcium hydroxide $CaOH_2$ in the noncarbonated samples. Contrarily the calcium hydroxide was not identified in the carbonated samples (Figure 5). The formation of greater amount of calcium carbonate instead of other carbonates can be associated to the high percentage of calcium in the ordinary Portland cement used in this work (Pereira & Cincotto, 2001). Such a result indicates the successful adsorption of CO_2 in the cement based matrix.

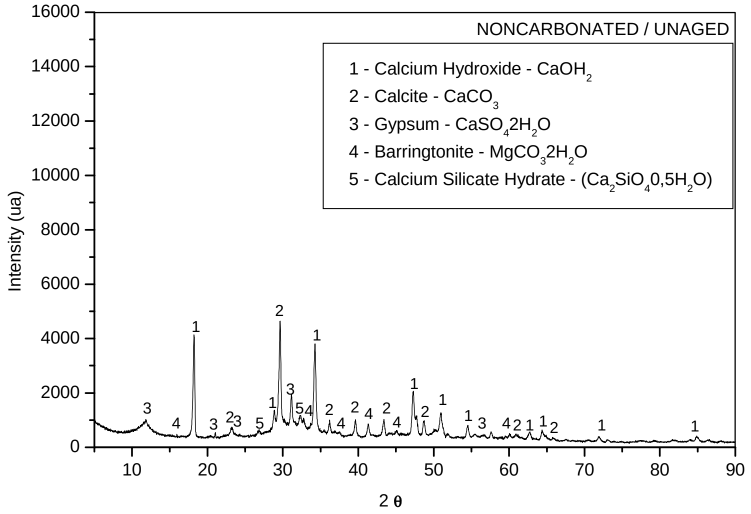

Figure 3 – X-ray diffraction pattern of the unaged and noncarbonated tiles.

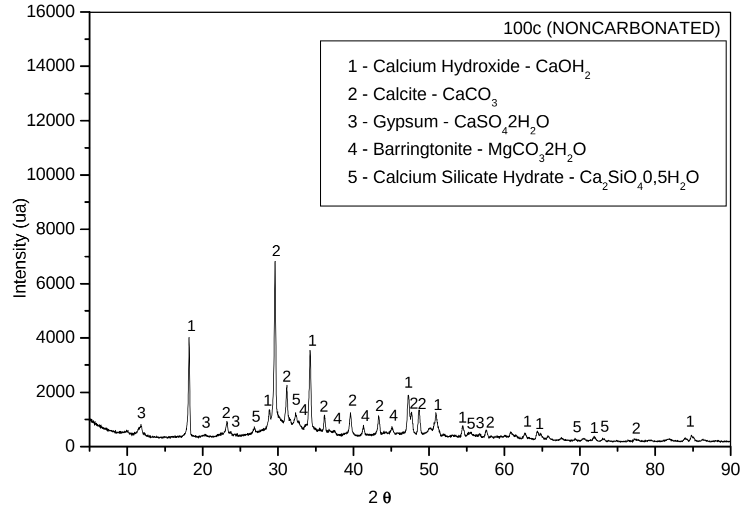

Figure 4 – X-ray diffraction pattern of the tiles after 100 ageing cycles (noncarbonated).

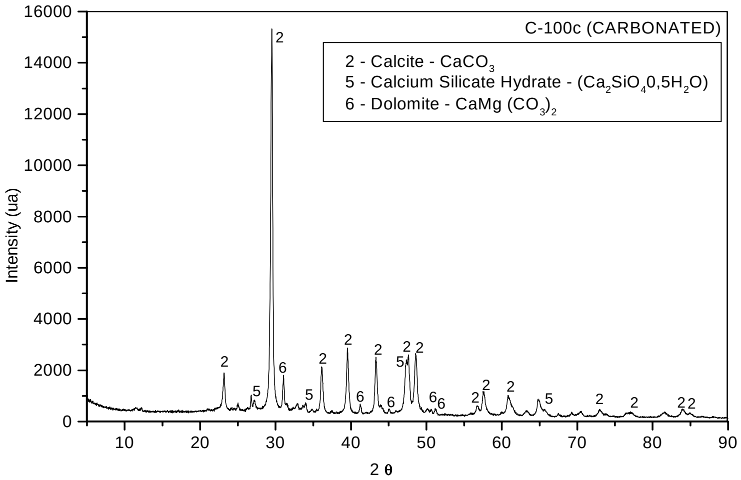

Figure 5 – X-ray diffraction pattern of the carbonated tiles after 100 ageing cycles.

The results of the potentiometric titration revealed a bit of production of $CaOH_2$ in the case of aged noncarbonated tiles in relation to unaged tiles. Besides, the chemical evaluation revealed about 98% of carbonates in the carbonated roofing tiles (C-100c) (Table 4). These results are in agreement with the X-ray diffraction patterns.

Such a behaviour is associated to the consumption of hydroxyls (OH) present in the cement matrix due to the adsorption of CO_2 after its diffusion into the pores of the composite. The high apparent porosity of the roofing tiles (around 40% at 28 days) has contributed to this fast diffusion (Taylor, 1997).

Table 4 – Percentage of calcium hydroxide and carbonate determined by potentiometric titration.

	% hydroxides	% carbonates
Noncarbonated / unaged	42.70 ± 0.40	57.30 ± 0.40
100c (noncarbonated-aged)	45.40 ± 0.70	54.60 ± 0.70
C-100c (carbonated-aged)	2.49 ± 0.02	97.51 ± 0.02

Series of carbonated roofing tiles after 100 ageing cycles (C-100c) showed the best mechanical performance in comparison to the other series (Table 3). It also presented significantly higher toughness (5.9 ± 1.9 kN.mm) in relation to those unaged and aged noncarbonated series.

Tolêdo Filho et al. (2003) have studied cement based composites reinforced with sisal and coconut chopped fibres. They achieved increase of the strength of the aged material and attributed it to the elimination of calcium hydroxide due to the carbonation treatment (109 days in a CO_2 incubator).

Silva (2002) reported the improvement of the mechanical performance of flat sheets reinforced with 12% by mass of eucalyptus pulp after accelerated carbonation and ageing cycles. No significant leaching was identified in carbonated products submitted to 40 ageing cycles.

Gram (1988) stated that the carbonation causes the reduction of the matrix alkalinity what was indicated as the major degradation factor of the cellulosic fibre constituents. The mechanical performance of carbonated composites was reported to be sustained even after accelerated ageing. This behaviour can be explained by the formation of calcium carbonate in detriment of calcium hydroxide.

However, the carbonated composites must be evaluated for longer periods of natural exposure. Mehta & Monteiro (1994) described the continuation of carbonation in environments with CO_2 excess and the generation of calcium bicarbonate. Consequently, as calcium bicarbonate is soluble in water, the performance of the roofing tiles can be prejudiced by the leaching associated to the incidence of rain water.

CONCLUSIONS

Accelerated carbonation provided the best mechanical performance for the roofing tiles. The content of calcium hydroxide in the carbonated tiles was smaller than in the noncarbonated ones. Reaction of calcium hydroxide with CO_2 gas has generated calcium carbonate and lower alkalinity of the cement matrix. Carbonated composites showed clear densification linked to the decrease of water absorption and apparent porosity. The improvement of toughness of carbonated tiles suggests that the fibres retained their capacity of reinforcement in the less aggressive medium. Potentiometric titration was an effective procedure to determine the percentage of carbonates formatted, as indicated by X-ray diffractions pattern.

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