Effect of the Accelerated Carbonation in Fibercement Composites Reinforced with *Eucalyptus* Pulp and Nanofibrillated Cellulose

Viviane C. Correia, Sergio F. Santos, Holmer Savastano Jr.

***Abstract*—**The main purpose of this work was verify the influence of the accelerated carbonation in the physical and mechanical properties of the hybrid composites, reinforced with micro and nanofibers and composites with microfibers. The composites were produced by the slurry vacuum dewatering method, followed by pressing. It was produced using two formulations: 8% of eucalyptus pulp + 1% of the nanofibrillated cellulose and 9% of eucalyptus pulp, both were subjected to accelerated carbonation. The results showed that the accelerated carbonation contributed to improve the physical and mechanical properties of the hybrid composites and of the composites reinforced with microfibers (eucalyptus pulp).

***Keywords*—**Carbonation, cement composites, nanofibrillated cellulose.

I. Introduction

CEMENT materials have low tensile strength and toughness, as a result of cracks formation when they are subjected to tensile loads. Cracking starts at the nanoscale and has a high impact on the durability of the matrix, because it facilitates the ingress of aggressive agents of the environment and reduces the potential performance of the building element and materials [1]. The incorporation of micro and nanofibers is a partial solution, because they act as bridge for transfer of stress, and is a solution to reduce the occurrence of cracking at early ages, improving the performance of these materials [2]-[5].

The carbon nanotubes have been incorporated into cement based composite as nano reinforcement to achieve relative high mechanical properties [2], [6], [7]. However, the use of vegetable fibers as reinforcement of the cement is an alternative due to their mechanical properties which provide improvements in ductility, flexibility and resistance to cracking of cement composites, besides it being abundant and renewable resource comparing to the synthetic fibers [8], [9].

The carbonation is the reaction of cement hydration products with carbon dioxide (CO_2). Accelerated carbonation of the cement materials can be employed to improve the durability of the cellulose fibercement composites, because it reduces the alkalinity of the cement matrix, lowering the pH and making it less aggressive to the cellulose fibers [10]. The reactions that occur during accelerated carbonation, provide the reduction of the porosity, water absorption, and become the cement matrix denser, which constitutes a positive process to improve the physical and mechanical properties of the composites [11]-[13].

The aim of this work was the production of the hybrid fibercement composites reinforced with bleached eucalyptus pulp and nanofibrillated cellulose (NC), and evaluates the effect of the accelerated carbonation in the physical and mechanical properties of the composites.

II. Materials and Methods

A. Nanofibrillated Cellulose (NC) Production

The bleached eucalyptus kraft pulp used to production of the NC and as micro reinforcement in the composites was provided by Fibria Celulose e Papel, situated at Jacareí city, Sao Paulo, Brazil.

The eucalyptus pulp was nanofibrillated at suspension water + pulp with consistency of 2% (w/w) by the grinding method. In this method the cellulose pulp was passed between a static grind stone and a rotating grind stone revolving at 1,700 rpm.

Eucalyptus pulp suspension was nanofibrillated using a commercial grinder Supermasscolloider Mini, model MKCA 6-2, with two grinding stones of aluminum oxide (Al_2O_3), model MKGA 6-80#, produced by Masuko Sangyo Co., Ltda, Japan. The two grinding stones were placed one over the other, since the bottom stone is rotated and the top stone is static. The suspension was passed 20 times through the grinder in order to ensure the nanofibrillation.

B. Fibercement Composites Production

The hybrid composites with eucalyptus pulp + NC were produced and compared to composites reinforced only with pulp, to verify the effect of the NC in the physical and mechanical properties of the composites.

The matrix was composed by Ordinary Portland cement (OPC) type CP V-ARI, correspondent to ASTM-C150 [14], Type I, and metakaolin 40 HP, provided by Metacaulim do Brasil, as pozzolanic material for partial replacement of the cement. The specific surface area and specific density of the metakaolin are 26.5 m^2/g and 2.6 g/cm^3 and of the OPC are 0.98 m^2/g and 3.10 g/m^3, respectively.

The composition of the fibercement is showed in Table I.

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TABLE I
FIBERCEMENT COMPOSITION

	Pulp (%)	NC (%)	Portland cement (%)	Metakaolin (%)
Pulp composite	9	-	75	25
Hybrid composite	8	1	75	25

The composites were produced in thin plates, measuring 200 mm x 200 mm x 5 mm. A slurry vacuum dewatering method, followed by pressing technique as adopted by Savastano Jr. et al. [15], was used to cast the plates. Some modifications were made from the original method to ensure maximum water removal of the composite during the production. The method is described below.

- Dispersion of pulp and NC in water under mechanical stirring during 5min;
- Addition of the Portland cement and metakaolin in the mixture of pulp + NC and pulp dispersed;
- Drainage of water from the suspension after it being transferred to the molding box and then applying negative pressure of 80kPa;
- Manual densification and pressing at 5.0 MPa, during 10 min, to remove excess water.

The samples were cured in saturated air conditions (i.e. sealed in plastic bags) under 25°C for 2 days, and then the samples were subjected to accelerated carbonation supercritical fluid in cylinder saturated with CO_2 at a pressure of 20 MPa in thermal bath at a temperature of 45°C for 1 h.

The thermal curing of the composites was completed inside a chamber at 45°C and 90% RH for 5 days. After curing the composites were subjected to physical and mechanical tests in the saturated condition.

C. Physical and Mechanical Tests

The eight specimens by formulation were subjected to non-destructive physical tests for determination of water absorption (WA), bulk density (BD) and apparent void volume (AVV) according to ASTM C-948-81 [16].

Mechanical tests were performed in the universal testing machine Emic DL-30000 equipped with 1 kN load cell. Four-point bending configuration was employed to evaluate the modulus of rupture (MOR), limit of proportionality (LOP), modulus of elasticity (MOE) and specific energy (SE) of the eight specimens by formulation, according to (1)-(4).

The SE was defined as the work carried out during the bending test and divided by the specimen cross-sectional area. The work was calculated by integration of the area below the load-deflection curve to the point corresponding to a reduction in the load carrying capacity to 90% of the maximum reached (4). A displacement rate of 1.5 mm/min was adopted in the bending test and the deflection was collected by the deflectometer positioned in the middle span, in the downside of the specimen. Pads were cut wet into four specimens with thickness of 5 mm, width of 40 mm and length of 160 mm using water cooled diamond saw.

$$MOR = \left[3 \,.\, P_{max} .\, (L_{\inf} - L_{sup})\right] / \left[2 \,.\, W \,.\, B^2\right] \tag{1}$$

$$LOP = \left[3 \,.\, P_{lop} .\, (L_{\inf} - L_{sup})\right] / \left[2 \,.\, W .\, B^2\right] \tag{2}$$

$$MOE = \left[(276 \,.\, L_{inf}^3)/(1296 \,.\, W .\, B^3)\right] .\, [P/\delta] \tag{3}$$

$$SE = [1/(B.W)] .\int P(\delta)d\delta \tag{4}$$

where P is load, P_{max} is the maximum load, P_{lop} is the load at the upper point of the linear portion of the load *vs* specific deflection curve (before the first cracking point), L_{inf} and L_{sup} are the inferior and superior span length, equal to 135 mm and 45 mm respectively, δ is the displacement registered by the deflectometer, B and W are the specimen thickness and depth (width) respectively. The load *vs* deflection curve was obtained to the point corresponding to a reduction in load carrying capacity to 5% of the maximum load. The specific deflection was calculated dividing the deflection by the length of the greater span (135 mm).

III. RESULTS AND DISCUSSION

This part comprehends the physical and mechanical results of the hybrid composites reinforced with pulp + NC, and also the composites reinforced with eucalyptus pulp, and show the influence of the accelerated carbonation in these materials.

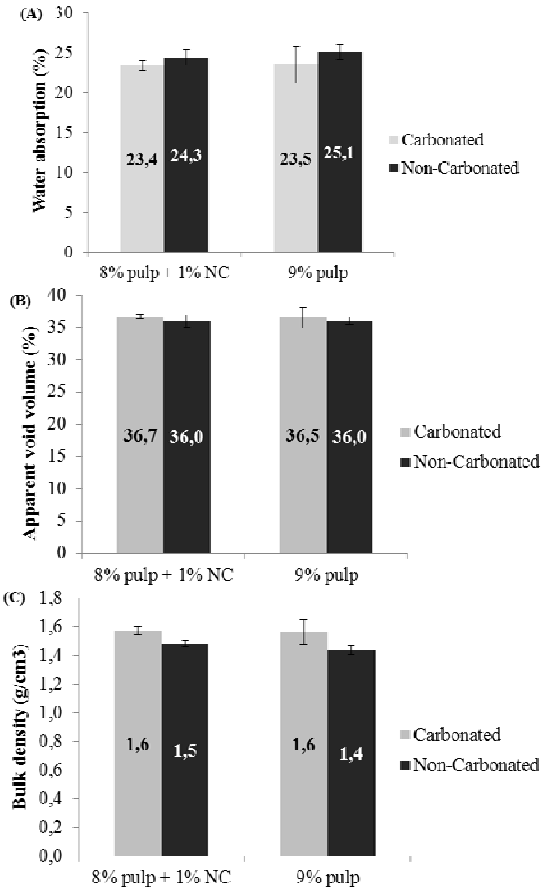

Fig. 1 Comparison of the effects of the accelerated carbonation in water absorption (A), apparent void volume (B) and bulk density (C) of composites with 8% of the eucalyptus pulp + 1% NC and composites with 9% of pulp

Figs. 1 (A), (B), and (C) show, respectively, the mean values and standard deviations of the physical characteristics of water absorption (WA), apparent void volume (AVV) and bulk density (BD) of composites reinforced with 8% of eucalyptus pulp + 1% NC, carbonated and non-carbonated and composites with 9% of eucalyptus pulp, carbonated and non-carbonated.

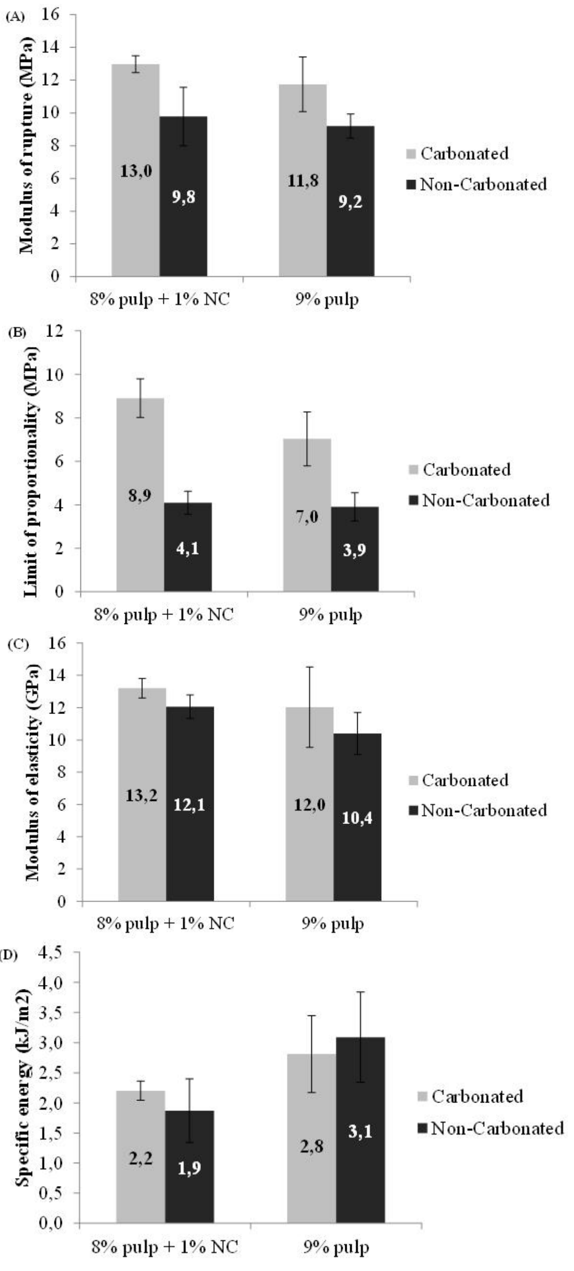

Fig. 2 Comparison of the effects of the accelerated carbonation in modulus of rupture (A), limit of proportionality (B), modulus of elasticity (C) and specific energy (D) of composites with 8% of the eucalyptus pulp + 1% NC and composites with 9% of pulp

The results show that using the accelerated carbonation as part of curing of the fibercement there was reduction in water absorption and higher matrix densification of the composite matrix with 8% of pulp + 1% NC and of the composites with 9% of pulp. According to Almeida et al. [17], carbonation reactions promote the filling of the pores in the matrix with carbonate products, which reduces apparent water absorption, apparent void volume and increase the bulk density, since calcium carbonate ($CaCO_3$) , produced from the carbonation is denser than calcium hydroxide ($Ca(OH)_2$) that is released in the hydration reactions of the cement.

The physical results showed no difference between the hybrid composites, with pulp + NC, and composites reinforced with pulp, so, the inclusion of NC had not a prejudicial effect in the physical behavior of the composites.

Figs. 2 (A), (B), (C), and (D) show, respectively, the mean values and standard deviations of the mechanical characteristics of modulus of rupture (MOR), limit of proportionality (LOP), modulus of elasticity (MOE) and specific energy (SE) of composites reinforced with 8% of eucalyptus pulp + 1% NC, carbonated and non-carbonated and composites with 9% of eucalyptus pulp, carbonated and non-carbonated.

The carbonation has contributed to improve the mechanical performance of the composite with NC and without NC. The carbonation favored the better behavior of the composite and of the matrix, and also the post-cracked condition. This behavior is attributed to the reactions that take place during carbonation, where there was the precipitation of calcium carbonate ($CaCO_3$) into the pores of the matrix. The calcium carbonate is denser than calcium hydroxide, so, occurs a greater densification of the matrix by reducing the pores of the matrix and it improve the fiber-matrix bonds and consequently the mechanical behavior of the fibercement [17]-[19].

Fig. 3 shows the typical stress x strain curves of the composites reinforced with 8% of eucalyptus pulp + 1% NC, carbonated and non-carbonated and composites with 9% of eucalyptus pulp, carbonated and non-carbonated. There is a clear increase of specific energy and LOP in the composites after accelerated carbonation, as a consequence of the matrix densification, and the increase in the strength of the composites, caused by carbonation.

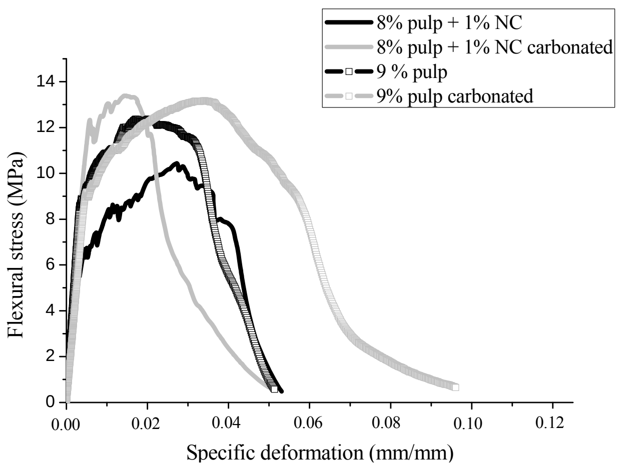

Fig. 3 Typical stress x strain curves at under flexure tests of the composites reinforced with 8% of eucalyptus pulp + 1% NC, and 9% of eucalyptus pulp in carbonated and non-carbonated conditions

IV. Conclusions

The physical and mechanical results demonstrated that accelerated carbonation is effective to improve the properties of the hybrid fibercement reinforced with fibers in micro and nanoscale and in composites reinforced with only pulp. The use of the NC to produce hybrid composites has not affected negatively the physical and mechanical performance of the composites subjected to carbonation.

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References

[1] Z. S. Metaxa, M. S. Konsta-Gdoutos, S. P. Shah, "Carbon nanofiber cementitious composites: Effect of debulking procedure on dispersion and reinforcing efficiency," *Cem. Concr. Compos*, vol. 36, pp. 25-32, 2013.

[2] G. Y. Li, P. M. Wang, X. Zhao, "Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes," *Carbon***,** vol. 43, pp. 1239-1245, 2005.

[3] R. D. Toledo Filho, K. Ghavami, M. Sanjuán, G. England, "Free restrained and drying shrinkage of cement mortar composites reinforced with vegetable fibres," *Cem. Concr. Compos*, vol. 27, pp. 537-546, 2005.

[4] F. Glasser, J. Marchand, E. Samson, "Durability of concrete. Degradation phenomena involving detrimental chemical reactions," *Cem. Concr. Res.,* vol. 38, pp. 226-246, 2008.

[5] A. Bentur, D. Mitchell, "Material performance lessons," *Cem. Concr. Res.,* vol. 38, pp. 259-272, 2008.

[6] G. Yakovlev, J. Keriené, A. Gailius, I. Girniene, "Cement based foam concrete reinforced by carbon nanotubes," *Mater. Sci.,* vol. 12, no. 2,pp. 147-151, 2006.

[7] M. S. Konsta-Gdoutos, Z. S. Metaxa, S. P. Shah, "Multi-scale mechanical and fracture characteristics and early-age strain capacity of high performance carbon nanotube/cement nanocomposites," *Cem. Concr. Compos.,* vol. 32, pp. 110-115, 2010.

[8] J. Claramunt, M. Ardanuy, J. A. García-Hortal, R. D. Toledo Filho, "The hornification of vegetable fibers to improve the durability of cement mortar composites," *Cem. Concr. Compos.,* vol. 33, pp. 586-595, 2011.

[9] M. Khorami, E. Ganjian, "Comparing flexural behavior of fibre-cement composites reinforced bagasse: Wheat and eucalyptus," *Constr. Build. Mater.,* vol. 25, pp. 3661-3667, 2011.

[10] R. D. Toledo Filho, G. L. England, K. Ghavami, K. Scrivener, "Development of vegetable fibre-mortar composites of improved durability," *Cem. Concr. Compos.,* vol. 25, pp. 185-196, 2003.

[11] M. Lesti, C. Tiemeyer, J. PLANK, "CO_2 stability of Portland cement based well cementing systems for use on carbon capture & storage (CCS) wells," *Cem. Concr. Res.,* vol. 45, pp. 45-54, 2013.

[12] S. A. S. Akers, J. B. Studinka, "Ageing behavior of cellulose fiber cement composites in natural weathering and accelerated tests," *Int. J. Cem. Compos. Lightweight Concr.,* vol. 11, no. 2, pp. 93-97, 1989.

[13] R. Macvicar, L. M. Matuana, J. J. Balatinecz, "Aging mechanism in celulose fiber reinforced cement composites," *Cem. Concr. Compos.,* vol. 21, pp. 189-196, 1999.

[14] ASTM C150/C150M-11. Standard. Standard Specification for Portland Cement; 2011.

[15] H. Savastano Jr., P. G. Warden, R. S. P. Coutts, "Brazilian waste fibres as reinforcement for cement-based composites," *Cem. Concr. Compos.,* vol. 22, pp. 379-384, 2000.

[16] ASTM C 948-81. Standard. Dry and wet bulk density, water absorption and apparent porosity of thin sections of glass-fiber reinforced concrete; 2009.

[17] A. E. F. S. Almeida, G. H. D. Tonoli, S. F. Santos, H. Savastano Jr., "Improved durability of vegetable fiber reinforced cement composite subject to accelerated carbonation at early age," *Cem. Concr. Compos.,* vol. 42, pp. 49-58, 2013.

[18] G. H. D. Tonoli, S. F. Santos, A. P. Joaquim, H. Savastano Jr., "Effect of accelerated carbonation on cementitious roofing tiles reinforced with lignocellulosic fiber," *Constr. Build. Mater.,* vol. 24, pp. 193-201, 2010.

[19] B. M. Fernández, A. Muntean, S. J. R. Simons, C. D. Hills, P. J. Carey, "A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO_2," *J. Hazard. Mater.,* vol. 112, no. 30, pp. 193-205, 2004.