EFEITO DA CARBONATAÇÃO ACELERADA EM COMPÓSITOS CIMENTÍCIOS REFORÇADOS COM POLPAS KRAFT[1]

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Resumo
O presente trabalho foi desenvolvido com o objetivo de obter compósito cimentício reforçado com polpas vegetais com maior durabilidade, através da realização da carbonatação acelerada em idades iniciais da hidratação do cimento. Os compósitos foram moldados em laboratório pelo processo de sucção a vácuo do excesso de água e posterior prensagem. Os compósitos foram carbonatados após dois dias de cura sob condições controladas de 60°C e 90% de umidade relativa. O trabalho avaliou o efeito da carbonatação acelerada nas características físicas e desempenho mecânico dos compósitos cimentícios. O estudo das propriedades microestruturais do compósito foi realizado por microscopia eletrônica de varredura ambiental e análise termogravimétrica. Resultados preliminares mostraram que a carbonatação acelerada nos primeiros dias de cura resultou em maiores resultados de propriedades mecânicas e na densificação da matriz, o que sugere que esse pode ser um procedimento promissor para aumentar a resistência mecânica em idades iniciais dos compósitos e reduzir a degradação das fibras celulósicas.
Palavras-chave: Compósitos cimentícios; fibras vegetais; carbonatação;

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Abstract
The current study has been carried out in the attempt to durable fibre-cement composites by means of accelerated carbonation in the early stage of cement hydration. Fibre-cement composites were produced by the slurry dewatering and pressing technique. Two days after moulding, the composites were carbonated under controlled conditions: 60ºC and 90% of relative humidity. The work evaluated the effect of the accelerated carbonation on physical characteristics and mechanical performance of the cementitious composites. Microstructure characteristics of the composite were studied by environmental scanning electron microscopy (ESEM) and thermal analysis. Preliminary results showed that the accelerated carbonation in the first days of cure improved the mechanical performance and resulted in a denser matrix, which suggests that it can be an effective procedure to improve initial strength of composites and to mitigate the degradation of cellulose fibres.
Key words: Cimentitious composites, vegetable fibers, carbonation.

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1 INTRODUCTION

Vegetable fibers derived from wood have increasingly been added to cimentitious composites. This addition can result in the improvement of mechanical properties and is important in the processing of fibercements. In addition, these pulps are derived from renewable resources. However, the long term durability is a problem due to deterioration mechanism of these natural fibres in the highly alkaline environment of the cimentitious matrix (SAVASTANO JR.; DANTAS; AGOPYAN, 1994 [1]). The carbonation can be a solution to mitigate this problem.

To summarize, the mechanism of carbonation can be described as the diffusion of CO_2 from the atmosphere through unsaturated pores of the cimentitious matrix. The CO_2 is dissolved in the aqueous phase in the pores and transformed into carbonic acid (H_2CO_3), which is dissociated in ions HCO_3^- and CO_3^-. Additionally, the calcium hydroxide ($Ca(OH)_2$) is dissolved in Ca^{2+} and OH^- ions, resulting in the precipitation of calcium carbonate ($CaCO_3$). The parametric study concerning the CO_2 reaction with each compound of cement was developed by Peter et al. (2008)[2].

Tonoli et al. (2010a)[3] evaluated the carbonation effect on the durability of cimentitious composites reinforced with Kraft sisal pulps when applied after 28 days. They concluded that this procedure improved the mechanical strength, decreased the calcium hydroxide content and a denser matrix was reported.

According to the literature, accelerated carbonation immediately after molding produces a higher strength of mortars (KLEM and BERGER, 1972[4]). The strength of the individual cement compounds submitted to accelerated carbonation immediately after mixing resulted in the high strength development of the silicate phases (BERGER and KLEM, 1972 [5]).

The objective of this research was to evaluate the influence of accelerated carbonation carried out in the first days after molding the composites on the mechanical, physical and microstructural properties.

2 MATERIAL AND METHODS

2.1 Material

The following materials and ratios in dry mass were used: 10% of unbleached eucalyptus cellulosic pulp, 77,2 % of Portland cement type CPV-ARI according to NBR 5733[6] (Type III cement according to ASTM C150[7]), and 12,8% of ground carbonate material. Chemical compositions (% by mass of oxides) of the cement and carbonate were determined using X-ray fluorescence spectrometry and are presented in Table 1.

Table 1 – Chemical composition of the cement and carbonate (% by mass of oxides).

	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	SO_3	MnO	P_2O_5	TiO_2
	(% em massa)										
Portland cement	63,5	3,1	19,4	4,1	2,3	0,2	1,1	3,0	-	-	-
Carbonate	39,1	8,9	9,0	2,2	1,2	0,1	0,4	-	<0,1	0,2	0,1

2.2 Experimental

Fiber reinforced cement composite plates measuring 200mmx200mm were prepared in the laboratory using a slurry vacuum de-watering followed by pressing technique (SAVASTANO Jr. et al., 2000[8]). The formulation was determined based on previous studies (TONOLI et al., 2009[9]; TONOLI et al., 2010b[10]).
Two procedures of cure were applied to the composites, as is described below:

a) The samples were placed in a climatic chamber at 60°C and 90% of relative humidity for two days. Following this step, the samples were taken out of the chamber and maintained in air saturated cure under 25°C until completed 28 days from manufacture. The accelerated carbonation was not applied to these samples.
b) The samples were placed in a climatic chamber at 60°C and 90% of relative humidity for two days. Following this, accelerated carbonation was applied to the specimens for three days, approximately. After this, they were kept in air saturated cure under 25°C until completed 28 days from manufacture.

The accelerated carbonation of the composites was performed in the climatic chamber, where cycles of CO_2 were released inside of it. The carbonation of the cement matrix was evaluated by dropping a solution of phenolphthalein, that is frequently used in analysis as an indicator of pH because its solution is brilliant red (or pink) in alkalis substances, for example the hydrated cement, and is colorless in acid substances indicating the carbonation of the cement matrix.

2.3 Mechanical and physical properties of the fiber reinforced composites

Mechanical tests were performed in a universal testing machine Emic DL-30.000 equipped with 1 kN load cell. A four-point bending configuration was employed to evaluate the composites. A span of 135 mm and a deflection rate of 1.5 mm/min were adopted in the bending tests to determine the the limit of proportionality (LOP), the modulus of rupture (MOR) and the modulus of elasticity (MOE) of the specimens, according to the equations (1), (2) and (3). The mechanical test procedures are described in details previously (SAVASTANO Jr.; 2000[11]):

$$LOP = \frac{P_{lop} \cdot L_v}{b \cdot h^2} \qquad \textbf{(1)}$$

$$MOR = \frac{P_{max} \cdot L_v}{b \cdot h^2} \qquad \textbf{(2)}$$

$$MOE = \frac{276 \cdot L_v^{\,3}}{1296 \cdot b \cdot h^3} \cdot (m) \qquad \textbf{(3)}$$

Where P_{lop} is the load corresponding to the upper point of the linear portion of the stress-strain curve. P_{max} is the maximum load, L_v is the major span, b and h are the specimen width and depth respectively, m is the tangent of the slope angle of the load vs. deflection curve during elastic deformation.

The specific energy (SE) was defined as the energy absorbed during the flexural test divided by the cross-section area of the specimen studied, as described elsewhere (TONOLI et al., 2007[12]) and adapted from RILEM[13]. The absorbed energy was obtained by integration of the area below of the load vs. deflection curve. The deflection occurred in the bending test was collected by the deflectometer placed under the center point of the specimen. The specific deflection values were calculated dividing deflection by the span of 135 mm, in the present work.
Bulk density (BD) and apparent void volume (AVV) values were obtained from the average of seven specimens for carbonated and non-carbonated composites, following procedures specified by the ASTM C 948 Standard[14].

2.4 Scanning electronic microscopy

The effect of the accelerated carbonation in the microstructure was examined using environmental scanning electronic microscopy (ESEM) of polished cross-section, in the gaseous analytical detector (GAD) mode. The preparation of the samples is described in Savastano Jr. et al. (2005)[15]. The fracture surfaces obtained after mechanical tests were analyzed using secondary electron detector (SE).

2.5 Thermogravimetry and derivative thermogravimetry

The hydration rate of cement can be evaluated by measuring the mass loss of hydrated samples up to 800°C. Thermogravimetry (TG) and derivative thermogravimetry (DTG) have been used for evaluating the nature of hydration products formed in cement-based systems (DWECK, J. et al. 2002[16]; FORDHAM and SMALLEY, 1985[17]). According to the literature, the different DTG peaks that have been reported when hydrated cement is heated in themobalance are[16] (FORDHAM, 1985):

1- 100ºC: dehydration of water pore
2- 100ºC-300°C: different stages of dehydration of C-S-H
3- ~500°C: dehydroxylation of $Ca(OH)_2$
4- ~700°C: decarbonation of $CaCO_3$

The preparation of the samples for TG study was carried out using agate crucible, in which the composite was manually ground until the size of particles was lower than 0.063 mm. For the prevention of carbonation and maintenance of relative humidity, all specimens were stored in the vacuum up to the time when the test started. The analyses were performed using a TGA 2050 Thermogravimetric Analyzer V5.1A equipment. The experimental conditions were: N_2 gas dynamic atmosphere (40 ml .min^{-1}); heating rate (10°C min $^{-1}$); platinum top-opened sample pan. The samples were heated in the range of 20–900°C at a constant rate. The $Ca(OH)_2$ was estimated from the weight loss measured in the TG curve between the initial and final temperature of the corresponding DTG peak.

3 RESULT AND DISCUSSION

Mechanical and physical properties were obtained after 28 days from manufacture. The correlation between MOR, MOE, SE and LOP and physical properties can be seen in Figures 1 and 2.

The carbonated composites exhibited higher values of MOR, MOE and LOP than the non-carbonated. SE values were slight superior to the non-carbonated composites, suggesting that the main mechanisms of toughness was the microcracks, due to the high average value of apparent void volume, and the pull-out of fibers, as will be discussed.

It is important to remember that MOR values indicate that the fibers and matrix are working together after the first cracking, as a result of the good adhesion between them.

The bulk density and apparent void volume are interrelated and their magnitude depends on the void volume present in the material. The carbonated composites showed greater bulk density, consequently, the apparent void volume was the lowest.

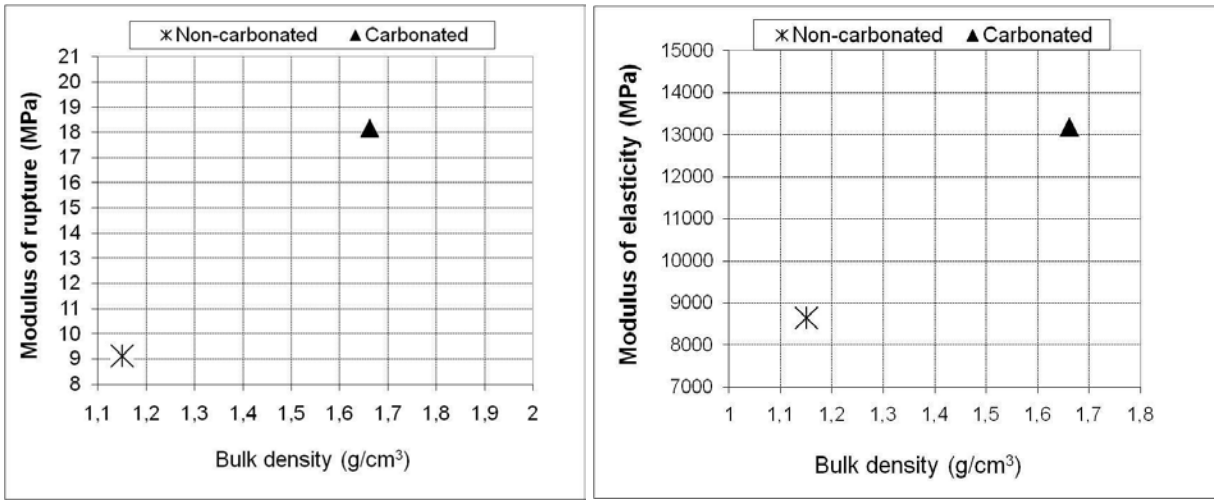


Figura 1. Average values modulus of rupture (MOR), modulus of elasticity (MOE) and and bulk density (BD) of the fibre–cement composites.

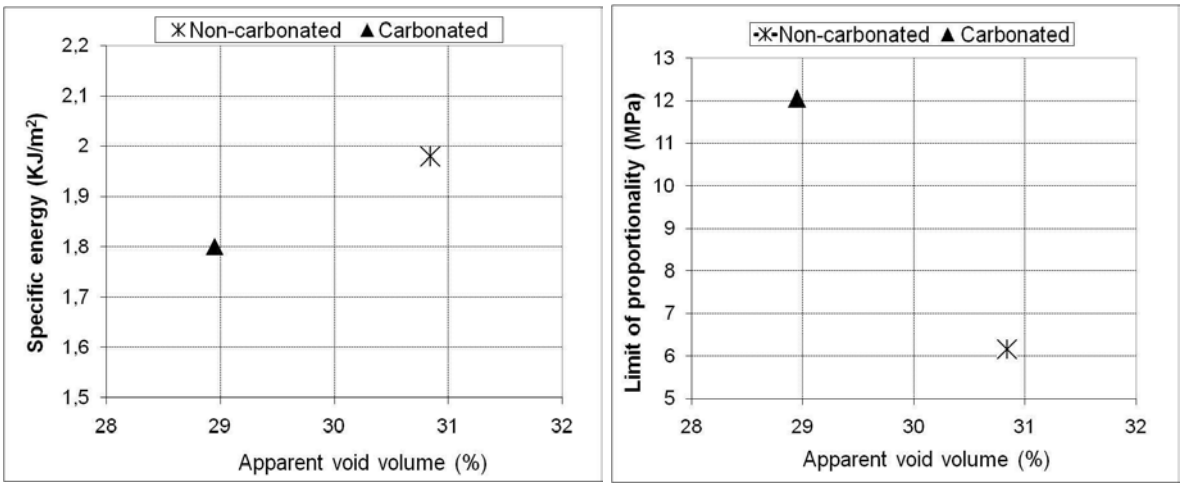


Figura 2. Average values of specific energy (SE), limit of proportionality (LOP) and apparent void volume (AVV) of the fibre–cement composites.

Micrographs shown in Figure 3 were obtained by scanning electronic microscopy of the fractured surfaces after mechanical tests. Considerations about cellulosic fiber and cimentitious matrix interaction can be suggested based on the analyses of these

images. The non-carbonated sample presented the fracture surface with a large number of pulled-out fibers from the matrix, due to the lower adhesion.
Carbonated sample presented minor number of pulled out fibers, showing a denser and compact matrix, resulting on a better adhesion and the improvement of the mechanical strength of the composites, mainly the MOR and LOP.

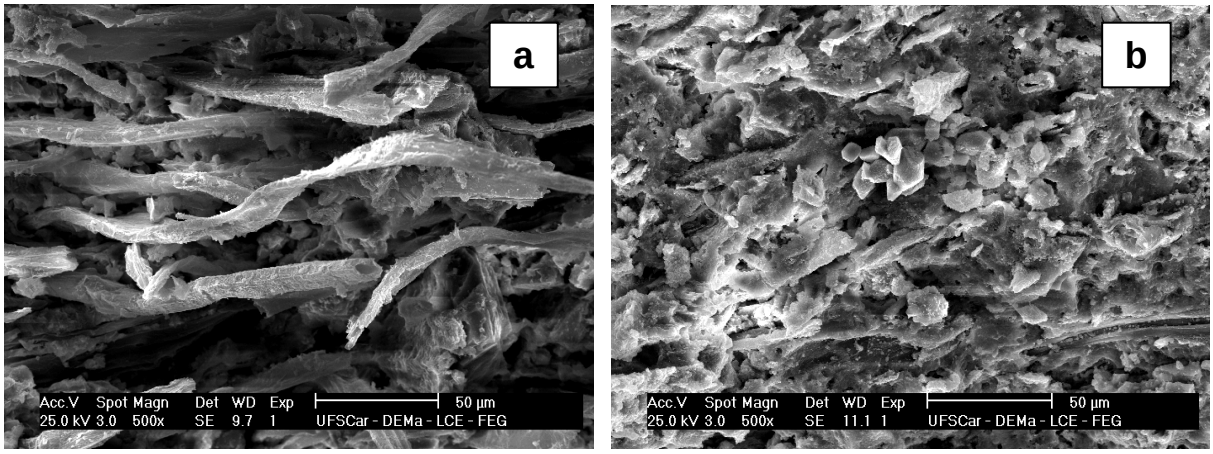
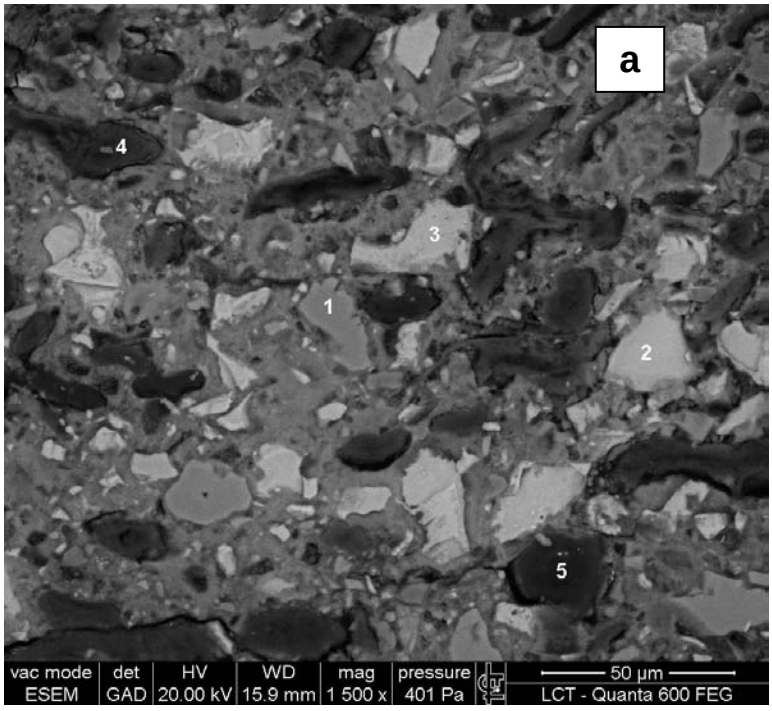


Figura 3. SE micrographs of the composite fracture surface (a) non-carbonated and (b) carbonated.

The polished cross-sections observed in Figure 4(b) show the microstructure of the carbonated specimen more homogeneous and compact than non-carbonated (Figure 4(a)), due to the lower quantity of voids represented by the darker irregular form, that is, voids filled by polymeric resin used to prepare the specimen to the analyses. The black elliptic form represents the cellulosic fiber. The cement hydrated products (gray tones) are better distributed in the carbonated specimen.



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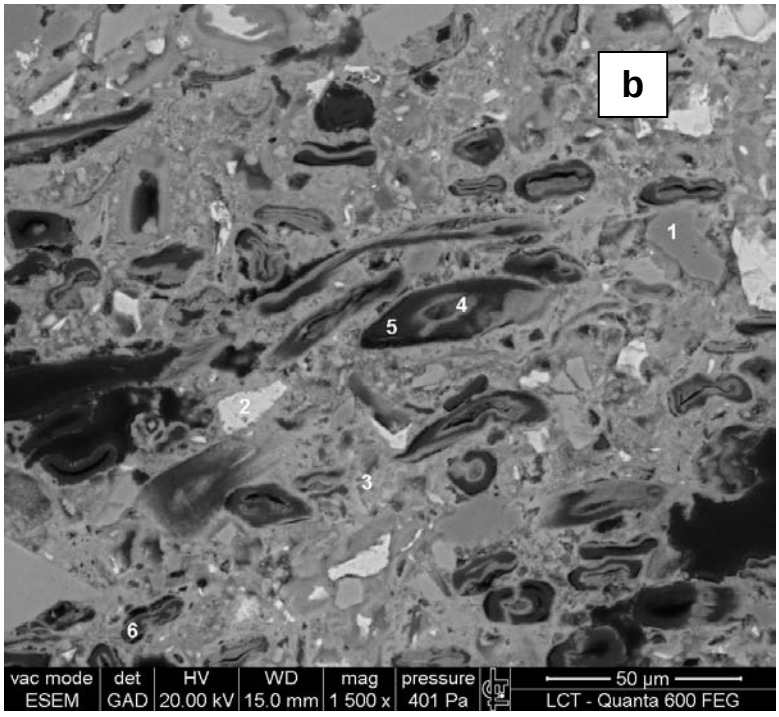

Figura 4. GAD micrographs of the polished cross-section of the composites (a) non-carbonated and (b) carbonated.

Figures 5 and 6 show the TG and DTG curves of the thermogravimetric analyses . According to the literature, weight loss in the peak of 450^{o}C showed in the DTG curve is reported as the dehydroxylation of the $Ca(OH)_2$. As can be seen, non-carbonated sample presented the peak and the carbonated did not, suggesting that the carbonation process reduced the $Ca(OH)_2$ content in the latter.

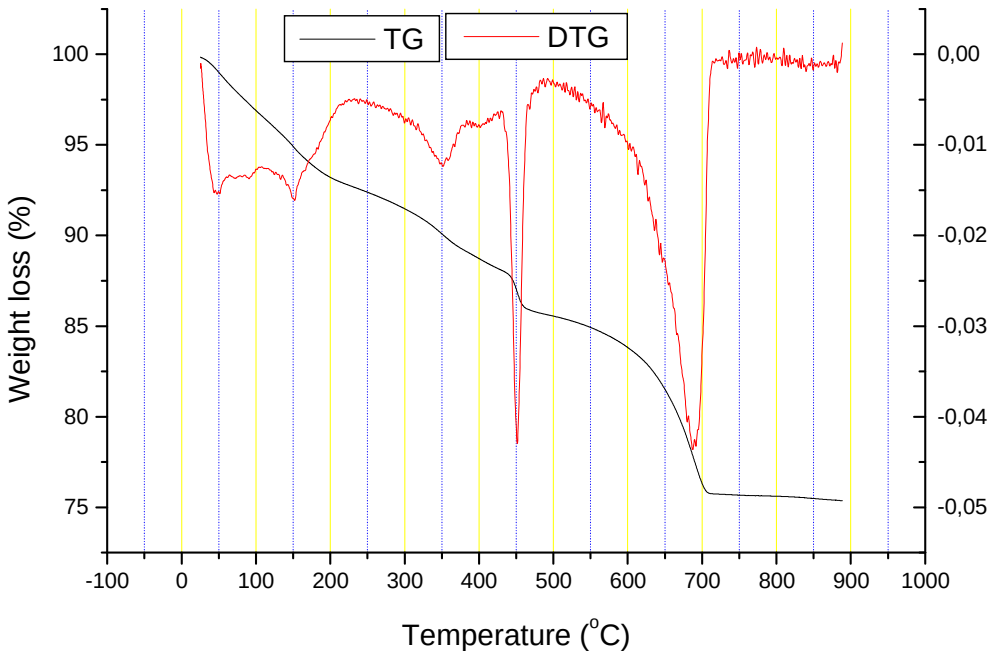

Figura 5. Weight loss of the non-carbonated composite.

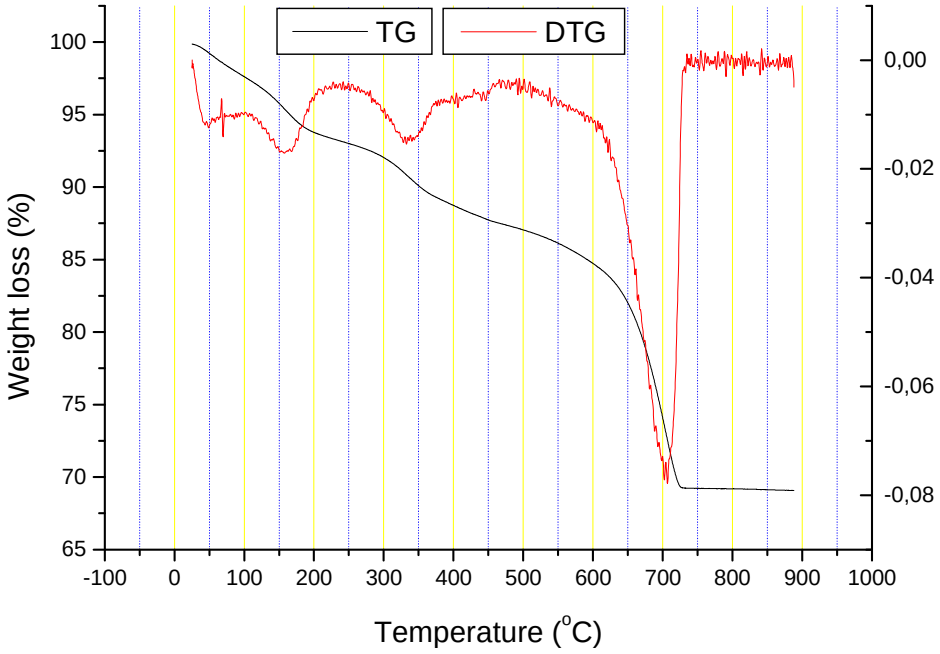

Figura 6. Weight loss of the carbonated composite.

4 CONCLUSIONS

According to the results, carbonated composites presented better mechanical properties than non carbonated ones. Accelerated carbonation resulted in the denser matrix, lower porosity and decreasing in the $Ca(OH)_2$ content. Furthermore, it was concluded that accelerated carbonation carried out in the initial ages (before 28 days from manufacture) has not caused a negative effect on the hydration process of cement, when it occurs in an accelerated way adopted in this work, that is, more concentrated than a natural condition.
The results presented are in agreement with the literature which has reported the effect of the accelerated carbonation as an improvement on the mechanical properties as a result of the densification of matrix and reduced $Ca(OH)_2$ content.

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