EVALUATION OF REINFORCED CEMENTITIOUS COMPOSITES WITH PINE CELLULOSIC PULP TREATED BY HORNIFICATION

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ABSTRACT

The use of vegetable fibers, as reinforcement of cement based inorganic matrices, is an alternative that has attracted interest by its economic, social and environmental performance. But their use is limited due to low durability displayed by composites, reflected by loss of resistance of vegetable fibers that are degraded by the alkaline environment of the matrix and the volumetric-dimensional instability. This paper discusses the potential of implement and evaluate the process of hornification (successive drying and rewetting cycles) on cellulosic pulp of pine (bleached and unbleached), as a treatment to allow for greater durability and stability of the pulp in cement-based matrix. Reinforced cementitious composites with untreated and treated pulps and evaluated their properties physical-mechanical until and after thermal cure and aging accelerated test were analysed. The results indicated that the previous treatment of fibers could have positive effects on the interface fiber-matrix without effects in the mechanical performance of the cementitious composites.

KEYWORDS:

Cement-based matrix; Vegetable fibers; Durability.

INTRODUCTION

In many countries around the world there is a strong trend to review the use of chrysotile asbestos, especially as reinforcement of inorganic cementitious matrices. To support this claim serious health problems derived from its manipulation are exposed. Nowadays asbestos free fiber cement products are already produced reinforced with other types of fibers (Harrison et al. 1999; Toloni 2009). One of these alternative fibers used as reinforcement of the cement matrix are vegetable fibers , which present interesting features, for example , their biodegradable behavior , low density and lower cost when compared with mineral and synthetic fibers, becoming highly productive and economic and environmentally profitable for the fiber cement industry. This type of fibers is found in abundance in nature, is renewable and has adequate mechanical properties for the proposed use (Agopyan et al. 2005; Roma et al. 2008; Savastano Jr et al. 2005; Claramunt et al. 2011).

The cement-based products exhibit fragile mechanical performance, but the use of vegetable fibers as reinforcements supposes certain advantages such as increased mechanical strength in addition to higher ductility and thermal conductivity decrease (Padilha et al. 2001; Caldas et al. 2009). However, the use of vegetable fibers in cementitious composites presents some difficulties associated to high alkalinity within the matrix, which creates a tendency of the fibers to the degradation of cellulosic material and thereby to loss of reinforcement properties. In addition, water absorption capacity of the fibers generates a self-swelling process within the composite. This dimensional variation primarily takes place during matrix curing process and it is characterized by a moist environment where the fiber absorbs water and subsequently a drying phase takes place with a water loss, causing its displacement from the walls of the cement matrix (Savastano Jr 2000; Caldas 2002).

Various treatments on plant fibers have been studied to modify their characteristics prior to their introduction in the cement matrix, improving their performance. Among the considered treatments, the process of hornification is highlighted, defined as a set of physical and chemical phenomena that occur during the dewatering of the fibers through the drying and rewetting cycles. These phenomena are associated to structural changes that happen in the polysaccharide chains, event that causes the rigidifying of the fiber, clumping and reduction of the ability to absorb water and swell without modifying their mechanical properties (Jayme 1944; Weise 1998; Dos Santos 2005; Claramunt et al. 2010; Köhnkea et al. 2010).

The reduction in water retention values of vegetable fibers opens up the possibility of causing favorable effects to cement matrix, because of the greater dimensional stability of the fibers, generating a higher adhesion between fiber-matrix and reducing the formation of incrustations of calcium hydroxide on both the surface and the lumen of the fibers, leading to a possible reduction of the degradation of cellulosic material in the cement matrix (Claramunt et al. 2011).

Within this context, the aim of this study was to assess the mechanical performance of cement matrices reinforced with bleached and unbleached pine fibers not subjected to 4 cycles of drying and rewetting before and after accelerated aging tests.

EXPERIMENTAL

Materials

Bleached Softwood Kraft Pulp and unbleached pine fibers Unbleached Softwood Kraft Pulp were supplied by private company. Bleached and unbleached pine pulp is presented in a dry sheet form with 10% RH. As cementitious matrix high strength Portland cement CPV-ARI (NBR 5733) and limestone were used.

Pulp Treatment

The hornification process of pine pulps consisted of 4 cycles of drying and rewetting, as follows: (1) pulp drying in an oven with air circulation at 60°C for 7h; (2) rewetting by immersion in water at room temperature for 15h; (3) disintegration of wet cellulose pulp in a disintegrator (3.000 revolutions – 10min) (ISO 5263-1 pulps – Laboratory wet disintegration); (4) pulp suspension filtering through a Buchner funnel equipped with a wire screen (150 mesh). At the end of the process (after 4 cycles), the fibers were stored in sealed plastic bags until their subsequent use (methodologies taken and modified from Claramunt et al. 2011).

X-Ray Diffractometry

To measure the crystallinity index of the cellulose pulp before and after the treatment, the technique of X-ray diffractometry (XRD) was used. The crystallinity index of cellulose pulps was determined using the empirical method suggested in Segal, 1959. This method consists in calculating the index of crystallinity for cellulose (Cr.I.), according to the following equation (1):

$$Cr.I : \frac{l_{002} - L_{am}}{l_{002}} x100 \quad (1)$$

Where l002 corresponds to the maximum intensity of diffraction (crystalline) of plane (002) at 2θ: 22.6° and Iam refers to the intensity of the background scatter (amorphous) measured at 2θ: 16.6°. The values l002 and lam were obtained directly from diffractograms of studied pulp.

COMPOSITES PRODUCTION

Composition of cementitious matrix

2 sets of samples composed of 16 specimens each were prepared. The purpose of this stage was to evaluate the behavior of composites reinforced with bleached and unbleached hornificated and untreated fibers, according to their mechanical properties and durability of the fibers before and after the test accelerated aging. One set was prepared with untreated pulp and the other one with hornificated pulp. 8 specimens of each series were subjected to accelerated aging treatment. The experimental composition of the specimens was fixed in mass percentages as follows: 68% cement, 27% limestone and 5% pulp.

Formation of flat plates

For the production and characterization of the composites, flat plates of cement with dimensions of 200 x 200 x 5 mm were molded. The method of production is based on raw materials mixing, excess of water vacuum drainage and subsequent mechanical pressing (3,5 MPa for 5 minutes) according to the procedure described by Eusebio et al, 1998. Dried pulps were previously dispersed in water by means of a pulp disintegrator at 3000 rpm for 10 minutes. Other inputs were added and homogenized for another 10 minutes using a high speed mechanical stirrer (1700 rpm). The formed suspension was transferred to a molding chamber. For each formulation, plates were pressed individually, and sealed in plastic bags in saturated conditions for two days and then submitted to thermal curing (controlled environment of 90% RH and 60°C) for 5 days. Upon completion of the cure, the plates were cut into four specimens (160 x 40 mm) with water cooled diamond saw. Series consisting of 8 specimens for each formulation were tested in the saturated conditions (immersed in water 24 hours before mechanical testing) and another series of 8 specimens were intended to accelerate aging.

Accelerated aging method

The specimens were subjected to accelerated aging by a procedure of immersion and drying to study the behavior of the cellulosic fibers after aging. This test was adapted from the standard EN 494 (1994), and carried out in a climatic chamber, (Marconi, model MA 035). Each cycle of complete immersion in water has a duration of 170 min. Heating cycle to 70°C ± 5°C is kept for the same period of time. A complete cycle is represented by a full period of immersion and drying. Between each period of immersion and drying there is an interval of 10 min. The specimens were subjected to 200 cycles of accelerated aging.

ESPECIMENS CARACTERIZATION

Mechanical characterization

The specimens obtained from flat plates were subjected to mechanical 4 point bending tests, using universal testing machine (Emic DL-30000 model), equipped with a 1 kN load cell and using a deflection speed of 5 mm / min, determining the values of a module of rupture (MOR), elastic modulus (MOE) and specific energy (EE). Setting test were adapted to recommended by RILEM Committee 49 TFR procedure (1984) and adapted by Junior Savastano (2000) for determination of specific energy.

Microstructural characterization

Samples of treated and untreated pulp were fixed on metallic support ("stub") using carbon double face tape. Then, the fibers were placed in a low vacuum scanning electron microscope (SEM), brand Hitachi - model TM-3000, coupled with x-rays microanalysis system by energy dispersive spectroscopy. Working with low vacuum allows observing the samples without metallic covering. A voltage of 15 kV was used. The images were formed by acquisition of backscattered electrons at different magnifications.

RESULT AND DISCUSSION

Physical characterization of cellulosic pulps

Table 1. Variation of the crystallinity index of cellulose pulps treated by hornification

Specimen of Cellulose Pulp	0 cycles	IV cycles
Pine Unbleached Pulp	64,09	62,82
Pine Bleached Pulp	67,44	66,71

X-ray diffraction was used for hornificated and non-hornificated milled pine samples (bleached and unbleached) aiming physical characterization of the pulps. The test results are intended to determine whether significant changes are displayed on the crystallinity content of the cellulosic material, considering that crystalline cellulose contributes to the improved performance of the mechanical properties of the fiber, like modulus of elasticity.

It can be seen in Table 1 that the levels of crystallinity for pine pulps (unbleached and bleached) before and after four cycles of drying and rewetting treatment. The Figures 2 and 3 exhibit the behavior of the XRD patterns of the pulps studied. In Figures 1 and 2 peaks are observed corresponding to the maximum intensity of diffraction of plane (002) at 2θ : 22.6 ° and the peak corresponding to the scattering intensity at 2θ bottom : 16.6 °.

The highest levels of crystallinity are produced by pine bleached pulp compared with the contents of unbleached pulp, with approximately 5 % lower, as shown in Table 1. Regarding the behavior of crystallinity after 4 cycles of drying and rewetting table 1 shows that after hornification treatment a similar conduct based on the decrease in the levels of crystallinity for both bleached pine pulp and unbleached is present . When compared with the literature Claramunt et al. (2010), similar results for bleached hornificated pine pulps after treatment are obtained, identifying a decrease in the level of crystallinity behavior. However, in the study it is clear that the reduction in the levels of crystallinity before and after treatment is very small and do not really represent a significant modification; suggesting that the crystalline cellulose pulps in this study were not degraded to a significant degree by their treatment.

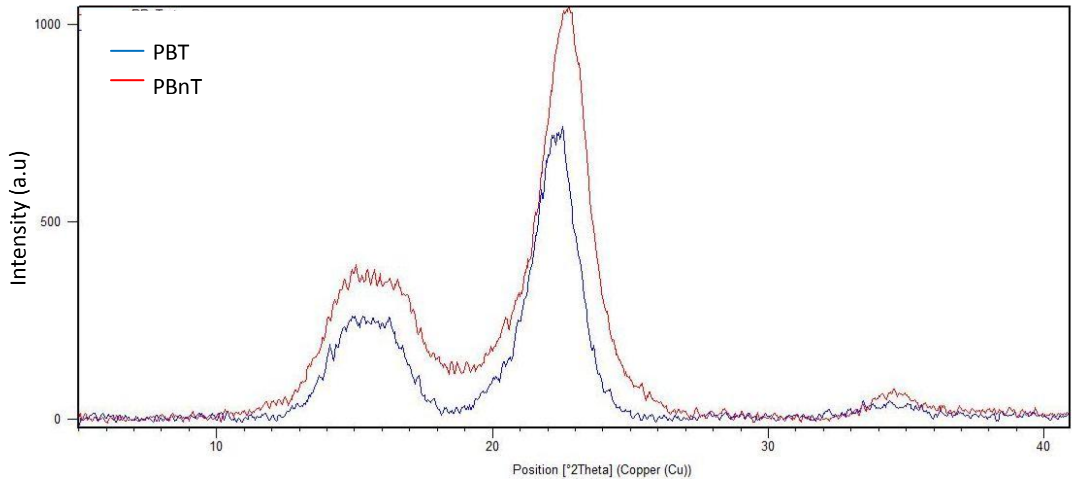

Figure 1. XRD behaviour of pine bleached treated and untreated

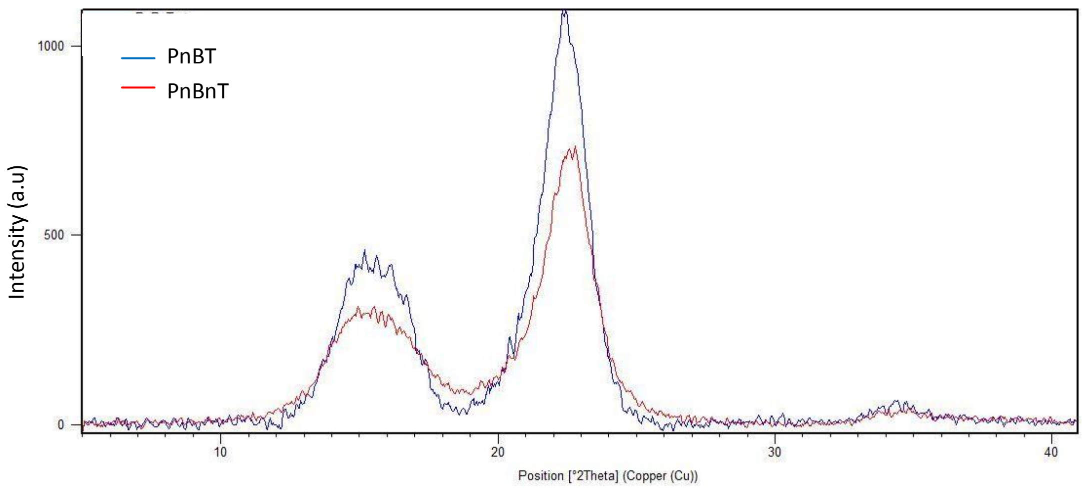

Figure 2. XRD behaviour of pine unbleached treated and untreated

Mechanical properties of composites reinforced with treated fibers

Typical behavior for tension-strain curves for the different studied formulations reinforced with treated and untreated milled pine fibers (a) bleached and (b) unbleached can be seen in figure 3.

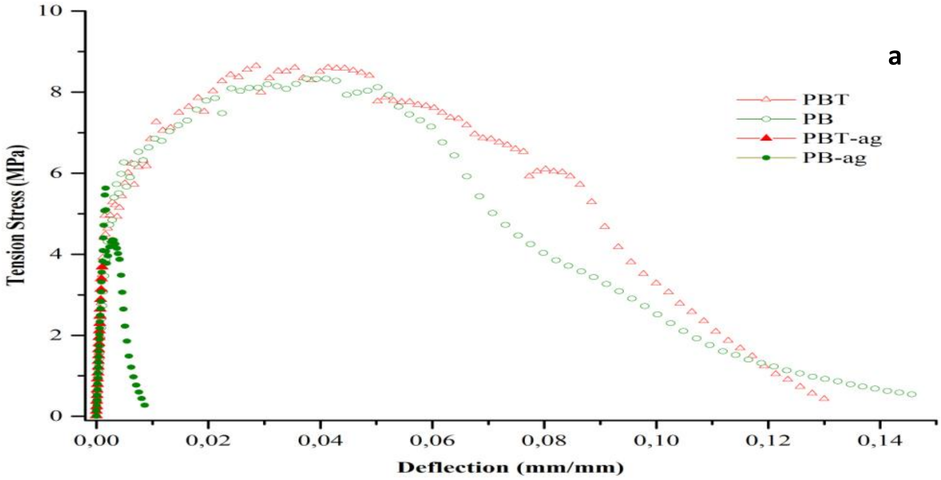

Figura 3a Typical stress-deformation curves for specimens reinforced by (PBT) pine bleached treated, (PB) pine bleached, (PBT-ag) pine bleached treated aged and (PBnT-ag) pine bleached untreated aged.

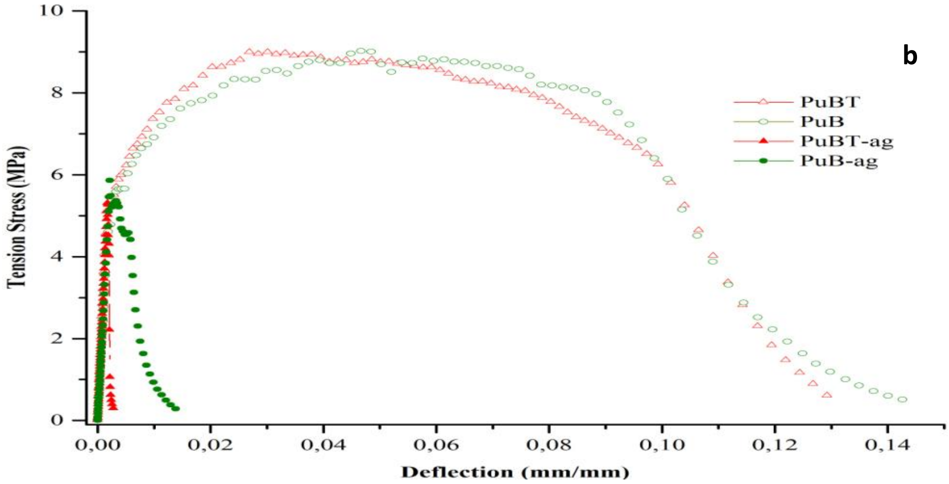

Figura3b typical stress-deformation curves for specimens reinforced by (PuBT) pine unbleached treated, (PuB) pine unbleached, (PuBT-ag) pine unbleached treated aged and (PuBnT-ag) pine unbleached untreated aged.

It firstly may be remarked the contribution of the cement matrix in the elastic region until the first cracking point and subsequently the effect of strengthening, contributed by vegetable fiber, originated by the transfer of loads from the matrix to the fibers and characterized by ductile performance (Hinoki et al. 2002) Displayed deformation after the first cracking point and the energy absorption by the fiber are consequence of the fiber reincforcement. The treated pine milled figure 3 (a) shows a similar behavior when compared with the untreated pine , moreover , it can be observed similarity between the maximum values of modulus of rupture, indicating that hornification is not deteriorating the fibers to the point of affecting this paramete, yet the hornificated milled pine is absorbing slightly higher energy. In Figure 3 (b) no significant difference was observed between the unbleached pine treated and untreated. Moreover, it can be identified that the unbleached pine has a higher value of energy absorption and therefore respond better to submitted stress. This situation can be explained by the fact that the unbleached pine did not suffer a bleaching process and therefore its physical and chemical structure is less degraded. As can be seen in Figure 3, the composites submitted to accelerated aging are presenting a loss of the ability to reinforce both bleached (a) and non- blanched fibers (b), favoring the brittle behavior of the cementitious matrix that is represented by a drastic decrease in stress-strain curve immediately after reaching the MOR. This situation indicates that for the specific conditions of this study, with 200 cycles of accelerated aging by immersion and drying, aging appears to be very aggressive and treatment is failing to prevent the gradual deterioration of cellulosic fibers.

The results of the mechanical tests for the specimens studied are shown in Figure 4, where the average values for the modulus of rupture (a) modulus of elasticity (b) and specific energy (c) were calculated. These results are considered a way to evaluate the behavior of the cement matrix and the reinforcing effect of treated and untreated pulps. In Figure 4 (a) can be observed that the values of modulus of rupture exhibit similarities for the different types of pulps performance with a range of about 3% content between the treated and untreated formulations. Regarding the modulus of elasticity, in Figure 4 (b) is experiencing an increase in the average value of this property for both milled and non-milled pie, highlighting that this condition is most notorious for pine milled with an increase of approximately 14%, compared with 1% for pine unbleached. The specific energy showed in Figure 4 (c) exhibits an increase of approximately 3% for milled treated pine samples with respect to the untreated pulp. This behavior is opposite to that shown by unbleached pine pulp, where untreated pulp content is around 9 % higher when compared to the treated pulp. In general, although there are differences between the behavior of the properties for the 2 types of pulps studied, by applying the statistical test of Tukey, with a significance level of 5%, it was determined that there is no statistically significant variation in the average values of properties mechanical evaluated.

After accelerated ageing, a general decline in the values of the mechanical properties is present, a situation that was expected due to the degradation of cellulosic material by alkaline attack and stimulated by multiple aging cycles to which the specimens were submitted. At this point, modulus of rupture had a decrease of 34% for bleached treated pine compared to untreated. On the other hand, the hornificated unbleached and untreated pine pulp showed a more stable behavior, represented by the proximity of the values between the different formulations. Regarding specific energy, established as straight indicator of reinforcement efficiency of the fibers, showed a sharp decline in their average values, allowing a fragile behavior of the cement matrix, thus suggesting the loss of reinforcement capacity of fibers caused by degradation of the cellulosic material. In a previous research carried out by Claramunt et al. 2011, who worked with pine kraft and cotton pulp, it was found a decrease in the average values of the specific energy, but their results indicated a greater preservation of cellulosic material in composites prepared with hornificated pulps. This difference in fiber performance can be explained by the difference between the processes of accelerated ageing.

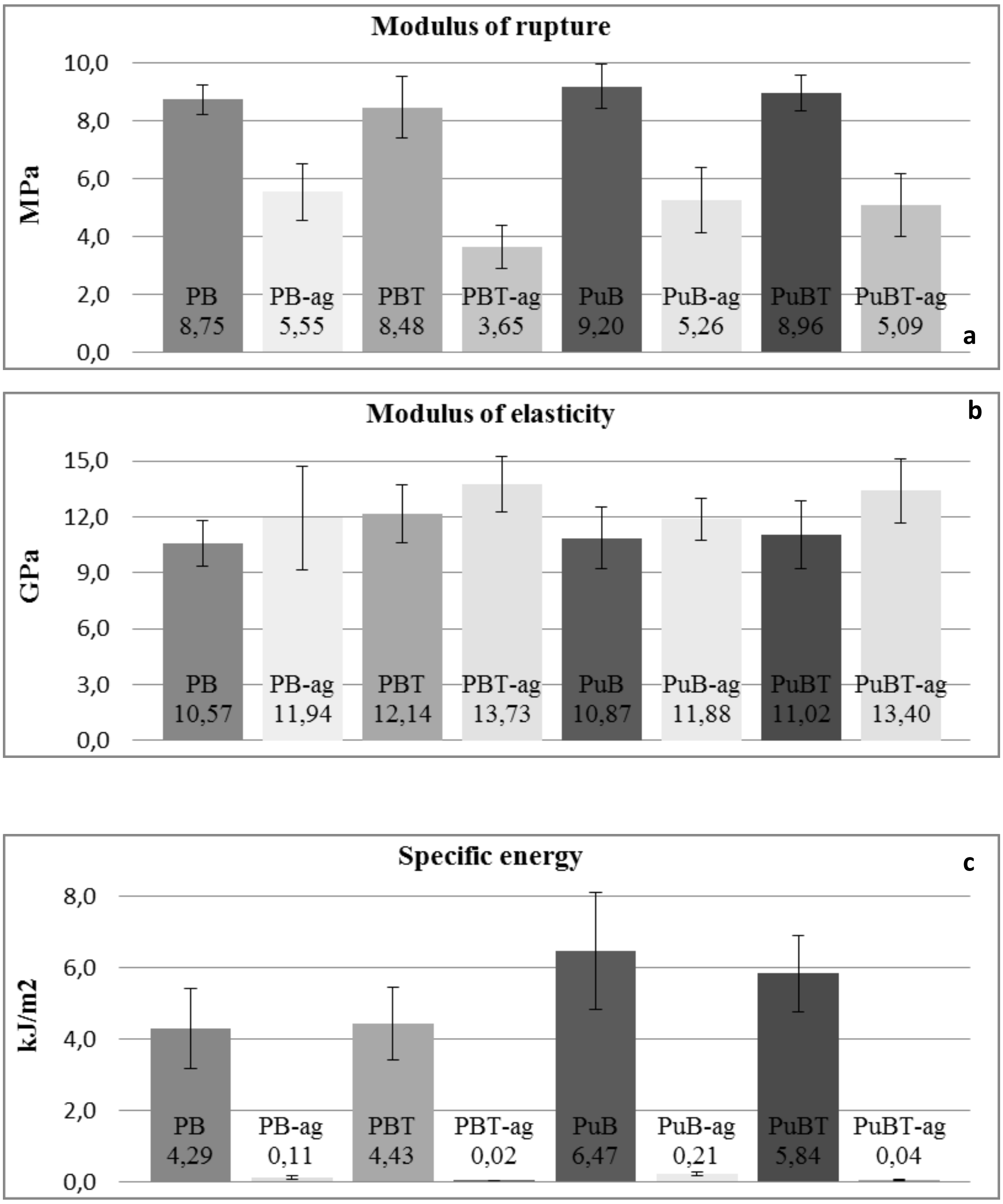

Figura 4. Average values of the mechanical properties (a) Modulus of rupture, (b) modulus of elasticity and (c) specific energy of specimens reinforced by (PB) pine bleached, (PB-ag) pine bleached aged, (PBT) pine bleached treated, (PBT-ag) pine bleached treated aged, (PuB) pine unbleached, (PuB-ag) pine unbleached aged, (PuBT) pine unbleached treated, (PuBT-ag) pine unbleached treated aged.

Morphological Characterization of Pulps

In composites reinforced with cement pulps, dimensional variation caused by pulps due to water absorption occurs. Vegetable pulps absorb the water present in the matrix during curing or after thereof hardening. This water uptake generates a swelling which causes the detachment of the pulp, generating a lack of adhesion between the fiber and the matrix, conducting the reinforcement to a loss of the capacity as reinforcement (Ferreira et al. 2012). Hornification process means an irreversible loss of the ability of water absorption of the fibers, based on the formation of hydrogen bonds in cellulose (Jayme 1944), moreover, is characterized by the breakdown and hardening the outer wall of the pulp. This could provoke a better adhesion between fiber and matrix by decreasing the swelling capacity. In Figure 5, SEM images magnified up to 1000x are presented. Figure 5 (a) shows a representative image of the region of the composites reinforced with hornificated unbleached pine after the accelerated aging process. In this image, it can be seen clearly fiber failure after bending test, evidencing a reinforcing action of the pulp. Moreover, good adhesion between the pulp and the matrix is observed, indicating that treatment is generating pulps with a better dimensional stability. On the contrary, in Figure 5 (b) is observed an image of the region of a composite reinforced with untreated milled and aged pine, where it can be seen a fracture with a poor fiber-matrix adhesion caused by the dimensional variation of the pulps, where it is clear that these were pulled out from the cement matrix during flexural test, leaving the space where they were. This behavior was observed for all formulations that used untreated pulps.

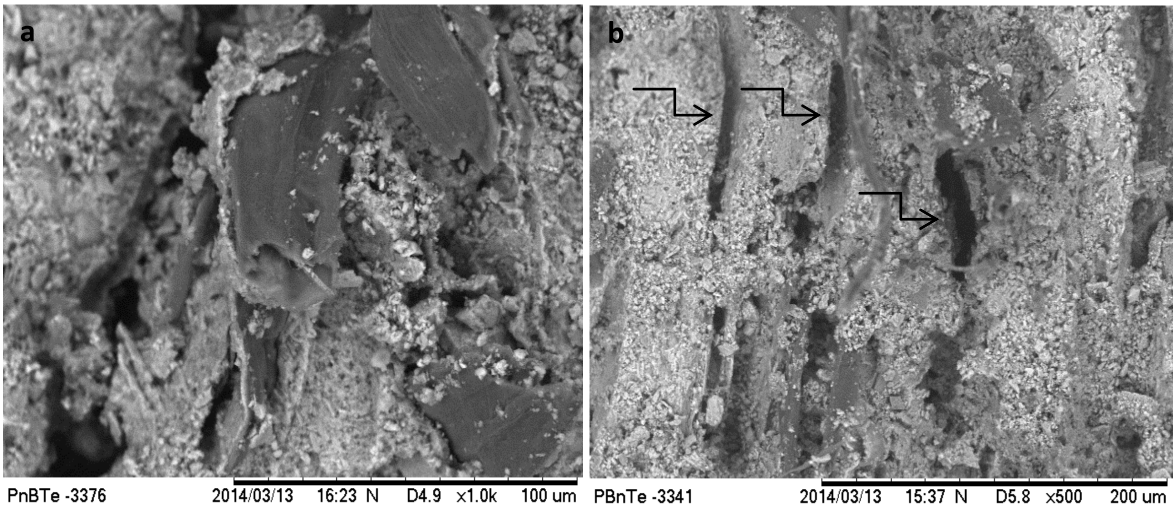

Figura 5. Images from scanning electron micrographs of (a) pine unbleached pulp treated – acelerate aging and (b) pine bleached pulp without treatement – accelerate aging (Magnification Range x 1.0k)

CONCLUSION

Based on the results obtained during the development of this work, it is possible to define some specific effects that the hornification treatment had on pulps and composite study:

- The contents of XRD suggested that hornification treatment based on 4 drying and rewetting cycles did not cause significant deterioration of the crystalline cellulose treated fibers.
- The average values of the mechanical properties of the different tested formulations showed a similar behavior for treated and untreated pulps. The values of the mechanical properties of the composites submitted to 200 cycles of accelerated aging have shown that the treatment is not effective to prevent the degradation of the pulp cellulosic material, which is reflected in specific energy decreases.
- The results suggest that treatment of hornification is generating greater dimensional stability and performance improvements in the fiber-matrix interface, but this statement must be proven by means of complementary tests as retraction test.

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