



Contents lists available at SciVerse ScienceDirect

## Composites: Part B

journal homepage: [www.elsevier.com/locate/compositesb](http://www.elsevier.com/locate/compositesb)

# Flexural properties loss of unidirectional epoxy/fique composites immersed in water and alkaline medium for construction application

Catalina Gómez Hoyos, Analía Vázquez\*

Polymer and Composite Materials Group, Institute of Engineering in Technology and Science (INTECIN), Engineering Faculty, University of Buenos Aires, National Research Council (CONICET), Las Heras 2214 (C1127AAR), Buenos Aires, Argentina

## ARTICLE INFO

## Article history:

Received 15 October 2011  
 Received in revised form 24 February 2012  
 Accepted 17 April 2012  
 Available online xxx

## Keywords:

- A. Polymer–matrix composites (PMCs)
- B. Mechanical properties
- C. Damage mechanics
- D. Mechanical testing
- E. Pultrusion

## ABSTRACT

Epoxy fique composites were evaluated for construction applications and compared with conventional wood used in construction. The composites studied were made with fique fibers treated using Na(OH) solution at 18 w/v%, untreated fique fibers were also used. The matrices were epoxy and epoxy with 5 wt.% of chemically modified C30B montmorillonite. Unidirectional composites of 90 mm × 20 mm × 4 mm were elaborated by pultrusion processing technique. The flexural properties loss occurred over 20 days of composites submitted to three types of environments: (i) water, (ii) saturated calcium hydroxide solution and (iii) mortar with w/c ratio of 0.45 and 540 kg/m<sup>3</sup> of cement, cured in a saturated solution of lime stone at 50 °C. Results showed that fiber treatment and montmorillonite addition improved the flexural modulus and strength of composites in 40% and 34% respectively. Moreover the flexural properties of composites before and after ageing resulted comparable or even better than conventional wood used in construction.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

Applications of natural fiber composites (NFCs) in construction are being investigated as a result of the increasing demand for environmentally friendly materials in construction. Applications like roof for housing [1–3], structural panels, unit beams [2,3], and door frames [4] have been investigated. Furthermore there are other applications in construction in which NFC could be a cheaper and environmentally friendly option. For instance NFC could be used to manufacture geocells used in treatments to control erosion of soil, or also in the manufacture of geotextiles used to separate, filter, reinforce, protect, and drain the soil. The knowledge of mechanical properties of NFC and their mechanical properties after exposition to both alkaline and humidity environmental or even mortar environmental is crucial for the acceptability of the NFC in construction applications. Since natural fibers may deteriorate in the highly alkaline environment of the cement matrix because dissolution of hemicellulose and lignin, affects the mechanical properties of composites [5,6].

Until now the researches about NFC, in construction [1–4,7], are focused principally on their processing and mechanical response, but their mechanical properties after exposition to alkaline or mortar environmental has not been studied. The use of polymeric

matrix as a binder around the natural fibers provides protection to them. However, if the interface of composites is not good, or the matrix is not alkaline resistant, the composite will deteriorate. When the molecules of H<sub>2</sub>O or Ca(OH)<sub>2</sub> enter in the NFC the following things could occur: (i) decrease in the mechanical properties of the matrix because, chains polymer hydrolysis, network swelling, relaxation and formation of hydrogen bonds between water and polymer molecules [8]. (ii) Deterioration of the interface, because H<sub>2</sub>O or Ca(OH)<sub>2</sub> could migrate at the interface. In the case of calcium hydroxide, the growth of its crystals in the voids of the interface may cause a severe damage to the composite [9]. (iii) Fiber swelling and embrittlement by chemical and biological attack [10].

To improve their mechanical properties of NFC before and after exposition to humidity and alkaline environmentals, both modification of natural fibers and modification of matrix can be carried out. Alkaline treatment of natural fibers appears as low cost alternative compared with other commonly used treatments such as: acetylation or silanization. Alkaline treatment results in bleaching of the fiber removing impurities, waxy materials, lignin and hemicellulose [10–12]. Regards to matrix modification, homogeneous dispersion and exfoliation of montmorillonite comes out as an attractive alternative. It has been reported that addition of montmorillonite reduces the coefficient of moisture diffusion, increases their mechanical properties, and improves significantly the mechanical strength [13,14].

Unidirectional composites with the matrix and the fiber modified and unmodified were elaborated by pultrusion processing

\* Corresponding author.

E-mail addresses: [cgomez@fi.uba.ar](mailto:cgomez@fi.uba.ar) (C. Gómez Hoyos), [avazquez@fi.uba.ar](mailto:avazquez@fi.uba.ar) (A. Vázquez).

technique. The flexural properties loss was measured after 20 days of ageing of composites submitted to three types of environments: composites in distilled water (pH = 6.0); composites in alkaline solution (pH = 12.0), to simulate the pore solution of cement mortar; composites included in cement mortar, cured in a lime stone saturated solution.

## 2. Materials and methods

This investigation uses Colombian fique fibers, extracted from the leaves of the fique plant *Furcraea Andina*, which is the most cultivated natural fiber plant of Colombia. Fique fibers were washed and dried before alkaline treatment to eliminate impurities and waxes of its surface.

The epoxy resin used as matrix (**E**) was diglycidyl ether of bisphenol-A (DGEBA) with  $n = 0.15$  and the hardener is triethyl-entetramine (TETA) from Hunstman and provided by Distraltec S.A. Argentina. The montmorillonite Cloisite 30B (**C30B**) was kindly provided by Southern Clay Products, Inc, USA. The Cloisite 30B is a group of mineral silicates which have been chemically modified with a quaternary ammonium salt (methyl tallow bis-2-hydroxyethyl).

### 2.1. Modification of fibers

The untreated fique fibers previously washed were treated with 18 w/v% NaOH solution at room temperature for 2 h, using a liquor ratio (fiber/solution w/v) of  $\frac{1}{4}$  (**FQ18**). After the alkaline treatment, fibers were rinsed with distilled water until neutral pH. Both untreated (**FQ**) and treated (**FQ18**) fibers were dried in an oven overnight prior to composite manufacture.

### 2.2. Modification of matrix

The unmodified matrix (**E**), was elaborated with the prepolymer DGEBA previously mixed with 12 wt.% of TETA. The modified matrix (**EC30B**) was prepared by mixing the prepolymer DGEBA with 5 wt.% of C30B for 30 min by means of a mechanical stirrer, followed for 30 min of sonication. Finally, the TETA hardener was mixed for 5 min by means of a mechanical stirrer.

### 2.3. Manufacturing of composites

Unidirectional composites were elaborated by manual pultrusion with around 40 wt.% of fique fibers. To elaborate the composite, the fibers proceeded through a bath, where they were impregnated with the matrix. Then the matrix-impregnated fibers were preformed to the shape of the profile. After that, the composite material was passed through a steel die that was machined precisely to the final shape of the composite manufactured. Finally the composites were submitted to following curing cycle: 21 h at 80 °C, then 15 h at 120 °C and finally 3 h at 140 °C. Samples with dimensions 90 mm × 20 mm × 4 mm were cut from the pultruded plaques to develop the mechanical tests and water absorption. Composites were identified using the name of the matrix used followed by the name of the fiber used.

## 3. Methods

### 3.1. Attenuated total reflection Fourier transforms infrared spectroscopy (FTIR-ATR)

Infrared spectroscopy experiments were developed using a FTIR spectrometer Nicolet 6700 Series equipped with a single-reflection Attenuated Total Reflectance (ATR) accessory. A type IIA diamond

crystal mounted in tungsten carbide of approximately 0.5 mm<sup>2</sup> sampling area was used. Infrared spectra were collected at 4 cm<sup>-1</sup> resolution using 64 scans.

### 3.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was developed using N<sub>2</sub> atmosphere at a heating rate of 10 °C/min, using around 14 mg of sample.

### 3.3. X-ray diffraction (DRX)

Powder X-ray diffractometry were carried out. DRX patterns were recorded by a SIEMENS D5000 diffractometer equipped with an X-ray generator operating with a curve graphite filter at radiation wavelength ( $\lambda = 1.542 \text{ \AA}$ ).

### 3.4. Field emission scanning electronic microscopy (FE-SEM)

Specimen surfaces were coated with a 30 nm gold layer and observed in a Field emission scanning electronic microscopy Zeiss Supra 40. Fiber and composite morphology were analyzed using FE-SEM operated in secondary electron mode under an accelerating voltage of 3 kV. The FE-SEM was performed on the polished and fractured surfaces of the composites.

Before FE-SEM analysis, surfaces of composites were studied using an optical microscope (Olympus PM63).

### 3.5. Energy dispersive X-ray spectrometer (EDX)

Energy dispersive X-ray spectrometer (EDX) attached to the SEM operated at 20 kV was used to characterize the diffusion of calcium hydroxide molecules in samples. All the composites were polished before the EDX tests.

### 3.6. Mechanical properties

Tensile tests of fique fibers were performed according to ASTM D3379 specification with a loading rate of 2 mm/min, using an Instron 4204 universal machine. About 20 fibers of 30 mm in length were tested. All tests were carried out at 25 °C.

Flexural tests of composites were performed in a Baldwin universal machine in three-point bending configuration of flexural stress, with 74 mm of support spam following the standard ASTM D790 M-93, Eq. (1) shows the bending equation. The specimen measures were: 90 mm × 20 mm × 4 mm and the crosshead speed was chosen in accordance with the standard.

$$\sigma = \frac{3PL}{2bd^2} \quad (1)$$

where  $\sigma$  is the stress in the outer fibers at midpoint;  $P$  is the load at a given point on the load–deflection curve  $L$  is the support spam;  $b$  is the width of the sample and  $d$  is the depth of the sample.

### 3.7. Flexural properties loss

The flexural properties loss occurred over 20 days of specimens stored at room temperature in three environments: (i) distilled water (pH = 6.0), (ii) saturated solution of Ca(OH)<sub>2</sub> (pH = 12.0) and (iii) cement mortar, cured in a lime stone saturated solution. The solutions were covered and the pH of the solutions was checked at regular intervals, solutions which had not retained the initial pH value were replaced. Changes in composites weight were followed over the time. After 20 days of ageing, samples were

rinsed with distilled water and let 7 days at room temperature until flexural test.

A conventional pan mixer was used to make the cement mortar, prepared following the standard EN 196-1, with w/c ratio of 0.45 and 540 kg/m<sup>3</sup> of cement. The curing process for cement mortar comprised three steps. In the first step, the specimens were molded and cured for 24 h at room temperature without moisture saturation. After that the specimen were demolded and stored in saturated calcium carbonate solution for 7 days at room temperature. Finally the specimens in the same saturated solution were held in a water bath at 50 °C for 4 days. Once completed the curing procedure composites were extracted from the mortar, rinsed with distilled water and let 7 days at room temperature until flexural test.

### 3.8. Water and calcium hydroxide absorption of composites

Composites absorption at time was calculated by the weight difference between pre-dried samples and samples exposed to water or calcium hydroxide. The weight changes with time were recorded. Samples were carefully dried with an absorbent paper prior to be weighed. The Eq. (2) was used to evaluate the weight gain of composites.

$$\%M_t = \frac{W_t - W_0}{W_0} \times 100 \quad (2)$$

where % $M_t$  is the increment in weight over time  $t$ ,  $W_t$  is the weight of the moist sample at time  $t$  and  $W_0$  is the weight of the dry sample.

### 3.9. Diffusion coefficients

The diffusion behavior of composites was evaluated by weight gain measurements of pre-dried specimen immersed in water or calcium hydroxide. The Fick's law was evaluated with following suppositions: the material is homogeneous; diffusion is the only mechanism involved in water absorption i.e. no chemical interaction between the polymer chains and water, without void content, etc. Therefore, the diffusion coefficient was used as fitting parameters in Eq. (3). This is the apparent diffusion coefficient, because takes into account all the involved mechanism in water absorption.

$$M_t = \frac{4M_m}{h} \left( \frac{t}{\pi} \right)^{0.5} D_{app}^{0.5} \quad (3)$$

where  $M_t$  is the increase in weight over time  $t$ ,  $M_m$  is the maximum weight gain;  $h$  is the thickness of the composites;  $t$  is the time and  $D_{app}$  is the apparent diffusion coefficient.

## 4. Results and discussion

### 4.1. Fique Fibers Treatment

The FTIR spectroscopy is an appropriate technique to establish the variations introduced by alkaline treatments on the chemical structure of the natural fibers. FTIR spectra of untreated and treated fibers are shown in Fig. 1. The spectra of cellulose hemicellulose and lignin were superposed to determine structural changes caused by their solubilization. It was found that peak around 2918 cm<sup>-1</sup>, corresponding to O–H stretching in methyl and methylene groups in cellulose hemicelluloses and lignin [15–18], was presented in all spectra. Moreover, after alkaline treatment some absorption decreased significantly. Absorption centered at 1735 cm<sup>-1</sup>, assigned to vibrations of acetyl and uronic ester groups of hemicellulose and ester linkage of carboxylic group of the ferulic and *p*-coumaric acids of lignin [15–17] decreased after alkaline

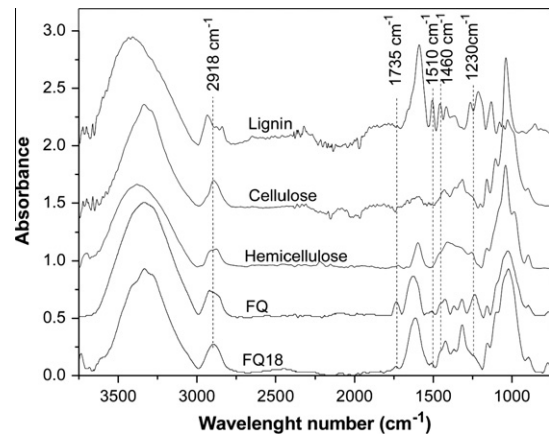


Fig. 1. FTIR spectra of: untreated fibers FQ, treated fibers FQ18, commercial cellulose, hemicellulose and lignin.

treatments. Furthermore, the band near to 1230 cm<sup>-1</sup> corresponds to stretching of ether groups of lignin and hemicellulose [15,16], also decreased significantly after alkaline treatments. This indicates that treatment removes appreciably the hemicellulose. In addition, spectra of both treated and untreated fibers exhibit some characteristic vibrations of lignin: 1510 cm<sup>-1</sup> (aromatic rings vibrations), 1460 cm<sup>-1</sup> (C–H deformations) [17,18], then treatment removes partially lignin from fiber structure. Lignin cannot be totally removed by the alkaline treatment, because lignin degradation is very difficult by presence of strong C–C linkages and aromatic groups, which are very resistant to chemical attack.

Fig. 2 shows the TGA curves which are used to characterize each compound in the fiber before and after alkaline treatment. The shoulder around 300 °C is because of hemicelluloses decomposition. Clearly, the alkaline treatment provoked an important loss of this compound. Peak at 360 °C is related to cellulose decomposition. Lignin was the most difficult to decompose, its degradation occurred slowly and appear as a wide peak from 200 to 600 °C. Its degradation is associated to dehydration, yielding derivatives structures, with lateral unsaturated chains releasing water, CO<sub>2</sub>, CO and CH<sub>4</sub> [19].

The XRD patterns are presented in Fig. 3. The diffraction patterns of FQ and FQ18 are very similar between them and exhibit several broad peaks. It can be found that the pattern of both fibers exhibits a sharp high peak at  $2\theta$  22.7° corresponding to 200 reflection plane and also the peak at the lowest angle can be described as

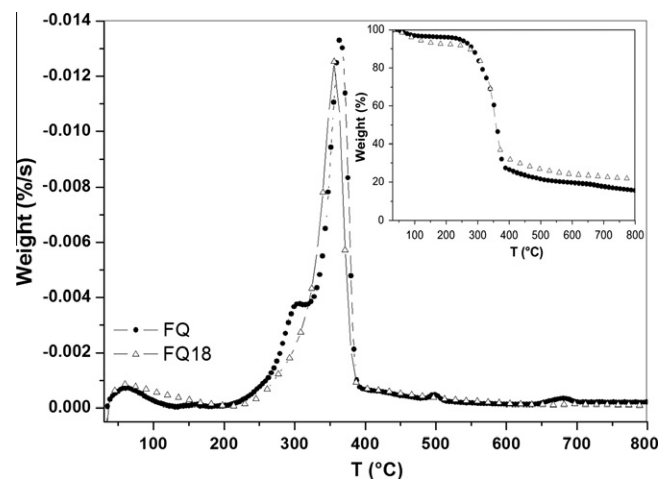


Fig. 2. TGA and differential TGA (DTGA) analyzes of untreated fibers FQ and treated fibers FQ18.

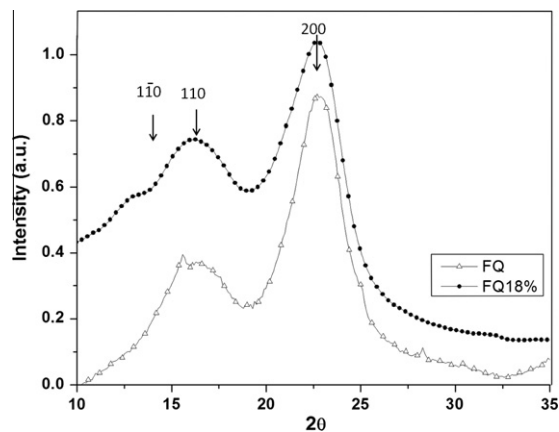


Fig. 3. DRX patterns of: untreated fibers FQ and treated fibers FQ18.

the overlapping of  $1\bar{1}0$  and  $110$  planes reflection at  $2\theta$   $15^\circ$  and  $16.3^\circ$ ; which are assigned to cellulose I [17,27]. For natural fibers like cotton and bamboo [27,28] have been reported that alkali concentrations higher than 16%wt. at room temperature and for 30 min or less, changes the fiber structure from cellulose I to cellulose II. However, for fique fibers treated with NaOH 18%w/v (15%wt.) for 2 h at room temperature alkaline treatment did not introduce changes in crystalline structure of cellulose, since both fibers exhibit very similar patterns.

The morphological changes in fibers were studied using FE-SEM. Fig. 4 shows the surface of treated and untreated fiber, both fibers exhibit a rough surface. However, treated fibers had more surface area available to contact with the matrix because exhibit some holes. For several vegetal fibers, alkaline treatment has been reported as an economical treatment that improves the interface between fibers and matrix. Since it removes waxy materials from fibers surface, increases its roughness and generates defibrillation, increasing the effective surface area available for contact with the matrix [12,20–23].

Furthermore, the treatment of fique fibers with solution of 18 w/v% NaOH resulted in important changes in their mechanical properties. As it is shown in Table 1, the alkaline treatment incremented the elastic modulus of fibers by 77%; and also increased their failure strength and failure strain by 64% and 17% respectively. Rong et al. [24] and Goda et al. [25] reported for sisal and hemp fibers respectively, that hemicellulose and lignin removal make the interfibrillar regions less dense and rigid, allowing fibrils to rearrange along the direction of tension, resulting in better load sharing.

**Table 1**  
Tensile properties of fique fibers.

Fiber	Tensile modulus (GPa)	Tensile strength (MPa)	Tensile strain (%)
Fique	$5.7 \pm 1.8$	$197 \pm 65$	$7.7 \pm 2.9$
Treated fique	$10.1 \pm 3.9$	$324 \pm 122$	$9 \pm 5$

#### 4.2. Composites

The silicates are modified through ion exchange reactions with quaternary alkylammonium cations to facilitate the intercalation of polymers into the interlayer galleries and therefore favor the formation of an exfoliated nanocomposite. The montmorillonite C30B was chosen because had been shown that modification with quaternary amines enhancing both the intercalation, and the interlayer spacing when is mixed with epoxy prepolymers [13,14,26]. However results showed that montmorillonite C30B was not exfoliated or intercalated because both composites with modified matrix exhibit a small peak in the same place that pure montmorillonite C30B (Fig. 5a and b). It is known that there are three main parameters which produce the clay exfoliation: (i) chemical compatibility between the particle and the matrix, (ii) time of sonication, and (iii) shear stress reached during mixing. In this research the chemical modification of the clay and the sonication time were selected as recommended other authors [13,14,26]. However the mechanical mixer was a simple mixer with low rpm (2000 rpm) which conduct to a low efficient mixing during the preparation of the composite.

Table 2 shows the mechanical properties of composites. The composite with treated fibers and modified matrix achieved the higher flexural properties; but the flexural properties increased more after fibers treatment than after matrix modification. Fig. 6 shows the pictures of composites obtained by optical microscopy. Comparing composites with modified and unmodified matrix we could see that, the modification of matrix with montmorillonite incorporated more voids into the matrix. Since montmorillonite addition produces an increment of voids due to its ability to air nucleation.

Fig. 7 shows the FE-SEM images of the fractured surfaces of the composites after mechanical test. Treated and untreated fibers showed good adhesion with matrix because of polar behavior of both fiber and matrix. Comparing both Fig. 7a and b we can observe that the surfaces of treated fibers shown in Fig. 7b seems more damaged than the surface of untreated fibers shown in Fig. 7a. Since as mentioned above, fibers treatment increases the surface area available to contact with the matrix and also increases

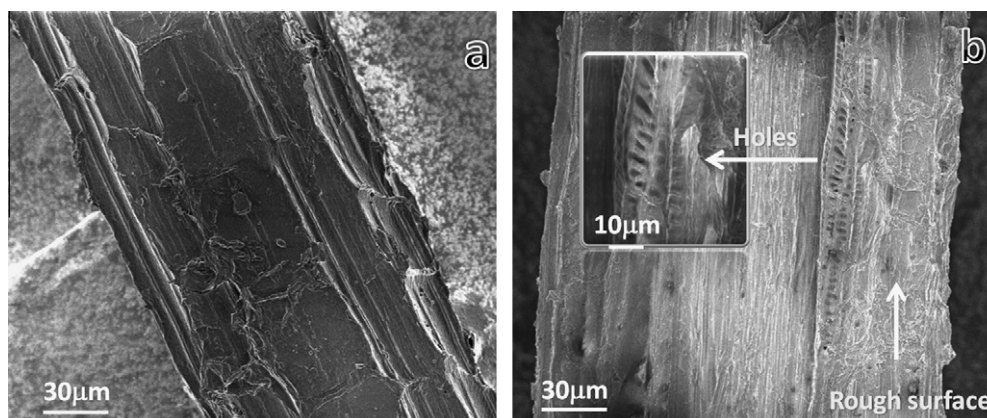
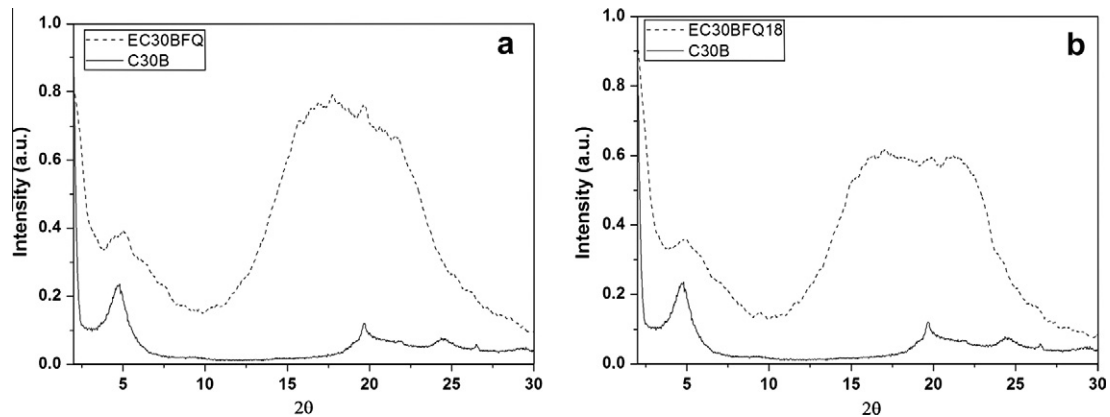


Fig. 4. FE-SEM images of (a) untreated fibers FQ and (b) treated fibers FQ18.



**Fig. 5.** DRX patterns (a) composites with unmodified matrix EC30BFQ and pure montmorillonite C30B and (b) composites with modified matrix EC30BFQ18 and pure montmorillonite C30B.

**Table 2**

Composites flexural strength before ageing in water or calcium hydroxide.

Specimen	Flexural modulus (GPa)	Flexural strength (MPa)	Flexural strain (%)
EFQ	5.7 ± 2.0	125.6 ± 26.7	3.0 ± 1.0
EFQ18	7.8 ± 1.3 (37%)	156.3 ± 13.5 (24%)	3.0 ± 0.6
E30BFQ	6.9 ± 0.8 (21%)	139.9 ± 14.5 (11%)	2.5 ± 0.3
E30BFQ18	8.0 ± 0.7 (40%)	168.3 ± 11.1 (34%)	2.7 ± 0.4

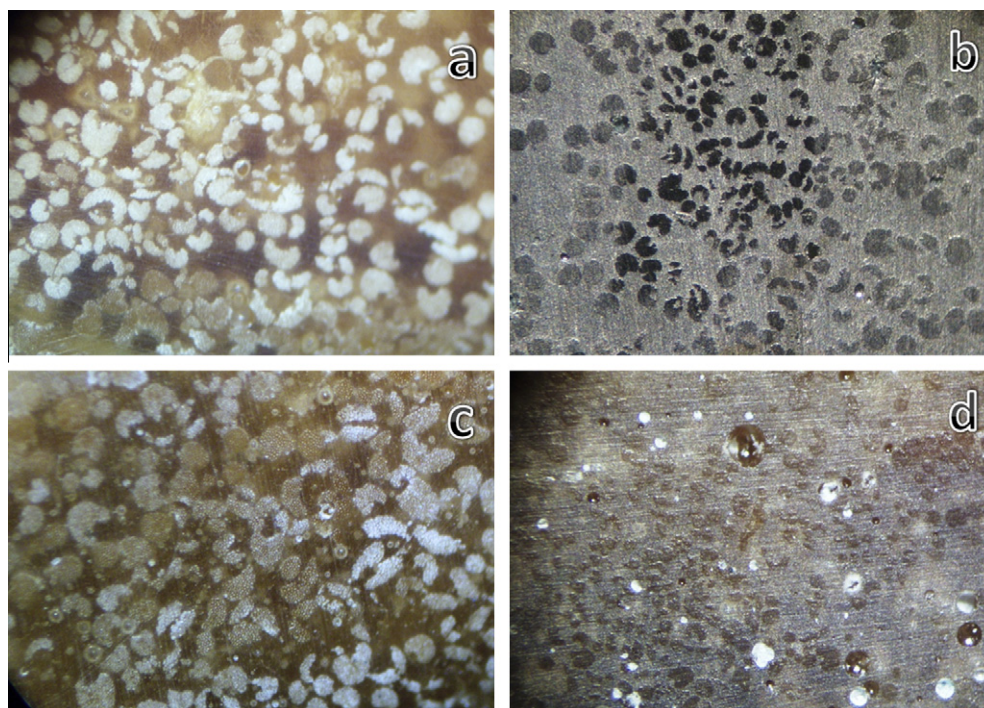
(%) improvements in mechanical properties respect to EFQ composite.

the accessibility of the hydroxyl groups in natural fibers [27–30]. Then the alkaline treatment on fibers increased the surface area to contact with the matrix and the available hydroxyl groups to interact with secondary hydroxyl groups of the crosslinked epoxy

resin. Additionally Fig. 8 shows the stress strain diagrams from flexural tests that also evidenced the improvements on interface after the alkaline treatment. Composites with untreated fibers presented pull out after break and reached lower tensile strength than composites with treated fibers.

#### 4.3. Water and calcium hydroxide absorption of composites

Fig. 9a and b, shows the percentage of both water and calcium hydroxide absorbed, plotted against time for all the matrixes and composites respectively. The same behavior was observed for all the composites. Composites absorb water very rapidly during the first stages reaching the saturation value, this initial behavior is linear in the beginning, after that absorption slows and approaches saturation, where no more is absorbed and the content of fluid in



**Fig. 6.** Pictures of composites obtained by optical microscopy: (a) EFQ (b) EFQ18 (c) EC30BFQ (d) EC30BFQ18.

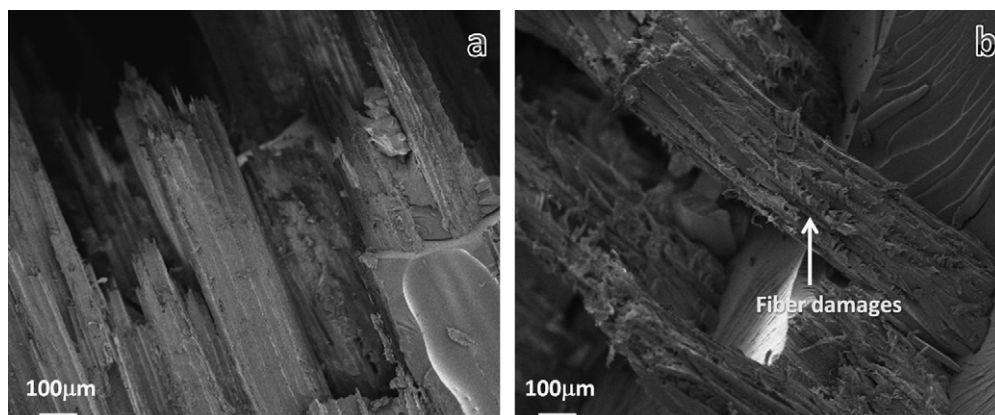


Fig. 7. FE-SEM micrographs of the fractured surface of composites with (a) untreated fibers EFQ and (b) treated fibers EFQ18.

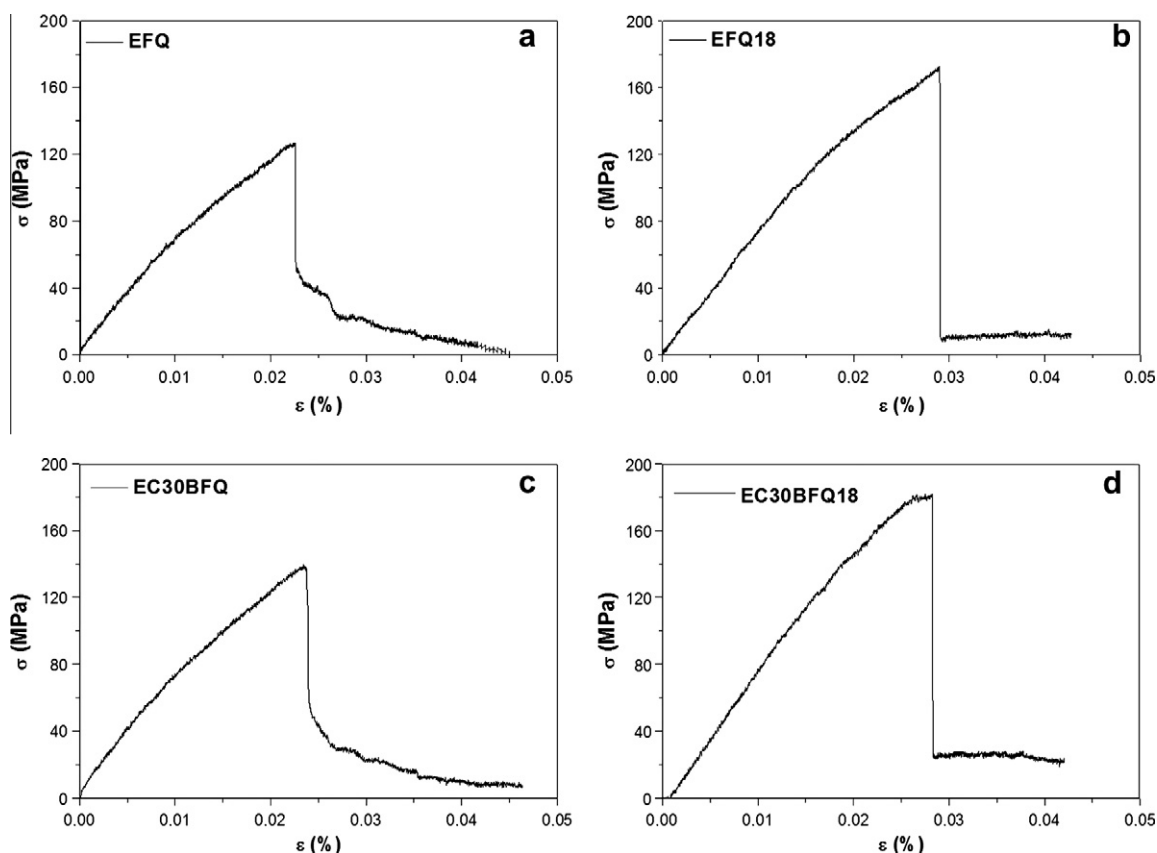


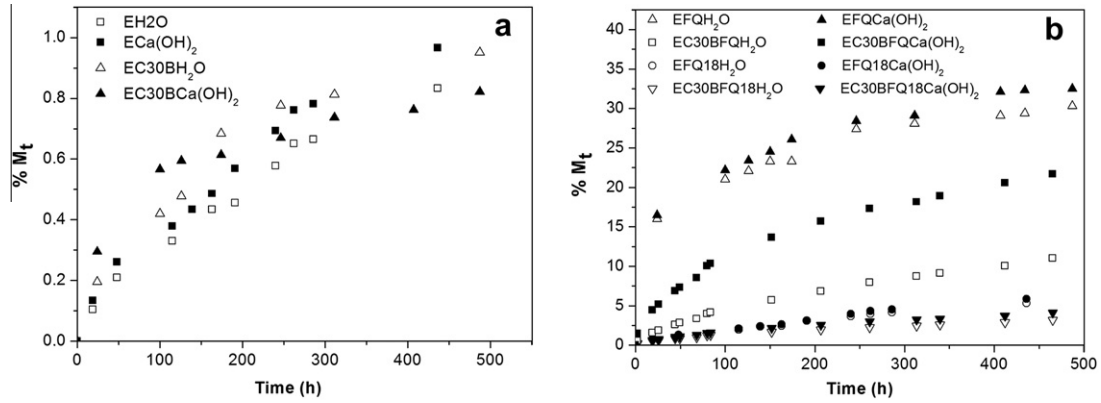
Fig. 8. Stress–strain diagrams of composites without absorption: (a) EFQ (b) EFQ18 (c) EC30BFQ (d) EC30BFQ18.

the composites remained the similar. Comparing composites with treated and untreated fibers, could be observed that fiber treatment decreased the absorption of both water and calcium hydroxide by around 6 times. Fig. 10a and b show the FE-SEM images of composites with treated and untreated fibers, composites with treated fibers shows less and smaller voids at interface than composites with untreated fibers.

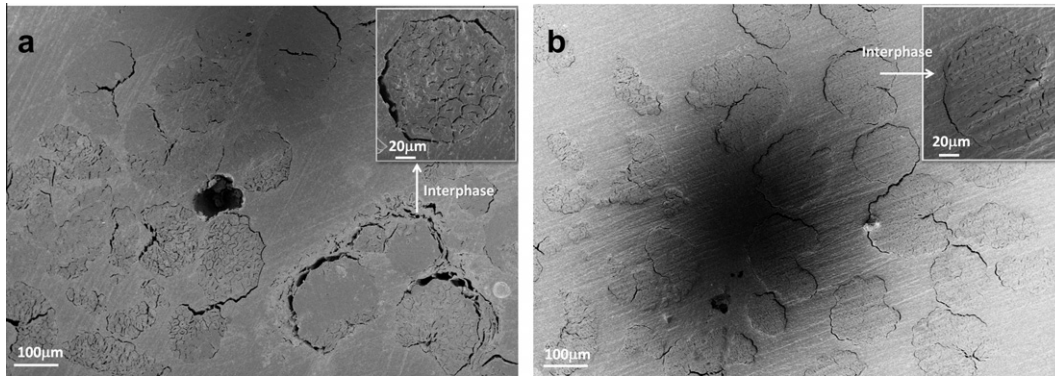
If there are voids in the matrix, the water goes into these voids and then passes through the solid matrix to the fiber/matrix interface [31]. Voids in the matrix could be produced during processing as a result of trapped air between the fibers, or also as a result of volatiles produced during curing of thermosetting resin. Interface also plays an important role in composites water absorption, since

if the interface is not perfect, the fiber and matrix can be detached and water gets into interface and then travel in axial direction of the composite because of fibers capillarity [33–35].

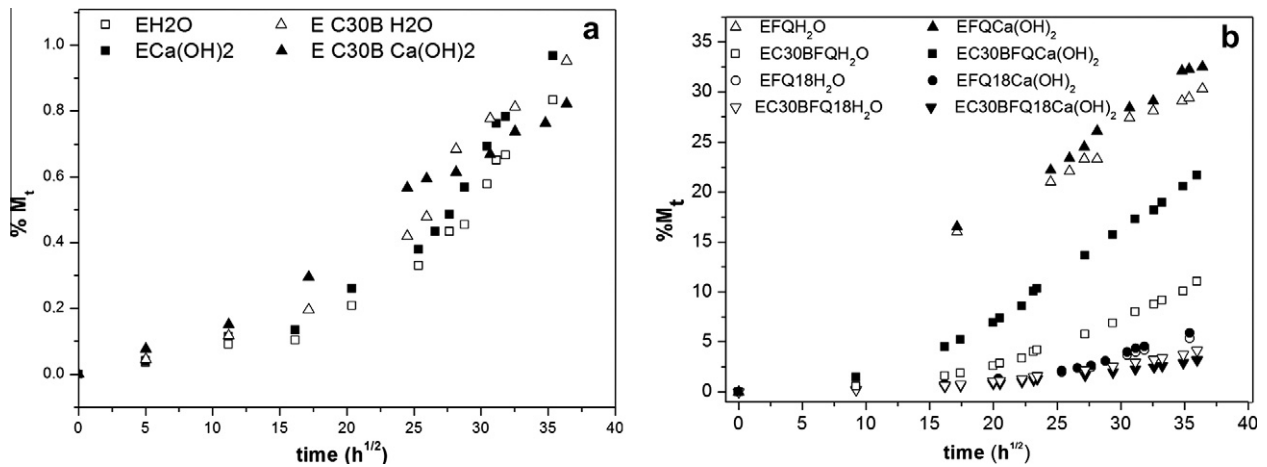
Comparing Fig. 9a and b, could be observed that the presence of natural fibers increased significantly the water absorption. The hydrophilic character is higher for natural fibers than for matrix; therefore matrix had little effect on the maximum amount of water or calcium hydroxide absorbed by composite. In addition, composites with treated fibers reached the saturation after 200 h, while composites with untreated fibers reached it after 300 h (Fig. 9a). Since capillarity that involves the water flow at interface between fibers and matrix, is stronger in composites with weak interfacial adhesion [31–33].



**Fig. 9.** Percentage of both water and calcium hydroxide absorbed, plotted against time of: (a) Matrices (□, ■ correspond to unmodified matrix; △, ▲ correspond to modified matrix) (b) Composites (△, ▲ correspond to composites with unmodified matrix and untreated fiber; □, ■ correspond to composites with modified matrix and untreated fiber; ○, ● correspond to composites with unmodified matrix and treated fiber and ▽, ▼ correspond to composites with modified matrix and treated fiber). The white shapes correspond to absorption in water and the black ones correspond to absorption in calcium hydroxide.



**Fig. 10.** FE-SEM micrograph of the polished surface of composites with (a) untreated fibers EFQ and (b) treated fibers EFQ18.



**Fig. 11.** Percentage of both water and calcium hydroxide absorbed, plotted against root time of: (a) Matrices (□, ■ correspond to unmodified matrix; △, ▲ correspond to modified matrix) (b) Composites (△, ▲ correspond to composites with unmodified matrix and untreated fiber; □, ■ correspond to composites with modified matrix and untreated fiber; ○, ● correspond to composites with unmodified matrix and treated fiber and ▽, ▼ correspond to composites with modified matrix and treated fiber). The white shapes correspond to absorption in water and the black ones correspond to absorption in calcium hydroxide.

#### 4.4. Diffusion coefficients of composites

Different mechanisms are active in moisture exposure of polymeric composite materials [33,34]: (i) capillarity mechanism that as mentioned above involves the flow of water or calcium hydroxide molecules into the interface between fibers and matrix; (ii)

transport by microcracks that comprises the flow and storage of water or calcium hydroxide in the cracks, pores or imperfections originated during the processing of the composite, as is the case of composites with modified matrix; (iii) diffusion of water or calcium hydroxide molecules inside the free volume between polymeric chains.

The value of the  $D_{app}$  shows the ability of water or calcium hydroxide molecules to penetrate inside the composite. It was calculated by considering the slope of the first part of the weight gain curve versus square root of time (Fig. 11) where Eq. (3) can be used.

Fig. 11 shows the percentage of weight gain as a function of  $\sqrt{t}$  for composites, as mentioned above these curves were used to fit the experimental data to Eq. (3) and calculate the  $D_{app}$ . Table 3 shows the values of the moisture diffusion coefficient obtained for the fitting of the linear part to Eq. (3). Espert et al. [33] and Joseph et al. [35] reported comparable values of the diffusion coefficient for sisal and polypropylene composites in water. The modification of matrix decreased values of the moisture coefficient. However composite with treated fibers and unmodified matrix reached the lowest diffusion coefficient value due to improvements at interface. Composites with treated fibers and modified matrix increased the values of the moisture diffusion coefficient, with respect to the composite with treated fibers and unmodified matrix. Since as mentioned above the modification of matrix introduced voids in composite that compromises flow and storage of water or calcium hydroxide.

Fig. 12a and b shows the EDX analysis for composites with modified and unmodified matrix. The composite with montmorillonite has the calcium hydroxide molecules concentrated at the edge exposed to the solution, because montmorillonite created a tortuous path and calcium hydroxide molecules cannot penetrate so easily in composite. While the composite without montmorillonite has calcium hydroxide molecules dispersed in composite.

#### 4.5. Flexural properties loss of composites after exposition to water and calcium hydroxide

Flexural test were performed in all the composites before and after water or calcium hydroxide absorption. Fig. 13 shows flexural properties loss of composites after exposition to water or calcium hydroxide. The flexural properties of composites decreased after a low value of absorption, because water or calcium hydroxide molecules change the structure and properties of the fibers, the matrix and the interface. For several natural fibers composites with polypropylene, unsaturated polyester and epoxy matrices have been reported that once water or molecules diffuse into the matrix, its glass transition temperature decrease and increase the rate of the diffusion [33,34,36].

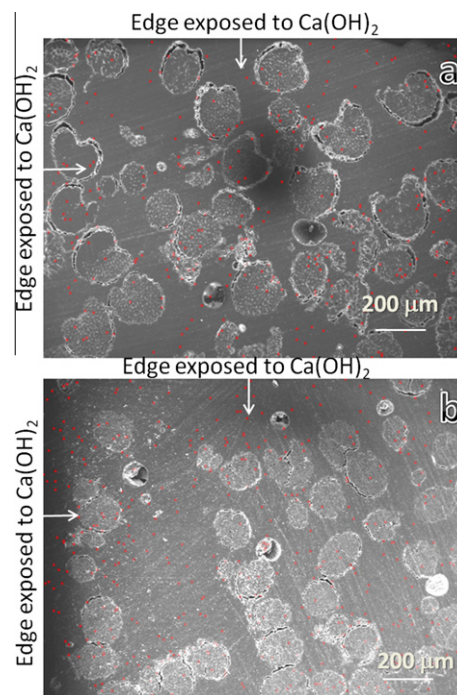
Flexural properties for all the composites were reduced after absorption of water or calcium hydroxide. This effect was more evident for composites with modified matrix, their flexural properties gets reduced in greater proportion respect to the composites with unmodified matrix. Therefore the voids introduced during the modification of matrix also favored the flexural properties loss.

In addition the loss in flexural properties depends on the absorption medium: water or calcium hydroxide. The flexural modulus for all composites (Fig. 13b) decreased more after exposition to calcium hydroxide than after exposition to water. Calcium hydroxide gets into the interface and makes that fibers become detached from the matrix; Purnell and Beddows [9] reported a similar behavior for composites with glass fibers. However the change in flexural strength is more complex. Fig. 13a shows that flexural strength gets reduced in greater proportion for the composites immersed in water than for the composites immersed in calcium hydroxide, except for composite with treated fibers, which behaves in opposite way. Since treated fibers were affected in more proportion for the dissolution of the cellulose and the remaining hemicellulose and lignin than untreated fibers. Qi et al. [14], observed for several natural fibers when are exposed to alkaline environments and water; water seems to be highly aggressive to lignin while alkaline environments seems to be highly aggressive to hemicellulose and cellulose.

**Table 3**

Absorption parameters of fique fiber composites aged in water and calcium hydroxide at room temperature.

Specimen/ environmental	Maximal moisture absorption $M_m$ (%)	Apparent diffusion coefficient $D_{app}$ ( $\text{mm}^2/\text{s}$ )
EFQ/H <sub>2</sub> O	30.3	1.01E–5
EFQ/Ca(OH) <sub>2</sub>	32.5	9.37E–6
EFQ18/H <sub>2</sub> O	5.32	9.53E–7
EFQ18/Ca(OH) <sub>2</sub>	5.87	8.93E–7
E30BFQ/H <sub>2</sub> O	11.01	1.05E–6
E30BFQ/Ca(OH) <sub>2</sub>	21.69	1.98E–6
E30BFQ18/H <sub>2</sub> O	4.11	1.21E–6
E30BFQ18/ Ca(OH) <sub>2</sub>	3.18	1.22E–6
<i>Matrices</i>		
E/H <sub>2</sub> O	0.83	7.0765E–7
E/Ca(OH) <sub>2</sub>	0.97	8.71288E–7
E30B/H <sub>2</sub> O	0.95	1.74742E–6
E30B/Ca(OH) <sub>2</sub>	0.82	4.1377E–6



**Fig. 12.** EDX analysis of (a) composites with unmodified matrix EFQ and (b) composite with modified matrix EC30BFQ. The red points represent the calcium hydroxide molecules. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The composite with treated fiber and unmodified matrix presented the better flexural properties after water or calcium hydroxide absorption. Their flexural properties remain higher than flexural properties for composite with untreated fiber and unmodified matrix even before absorption.

#### 4.6. Flexural properties loss of composites after exposition to mortar

Flexural test were performed in composites before and after inclusion in mortar. Composites were included in cement mortar with the aim to observe their flexural properties loss occurred over the time due to alkaline environmental generated by cement hydration. Table 4 shows the percentage of weight gained after inclusion in cement mortar. Composites with modified matrix



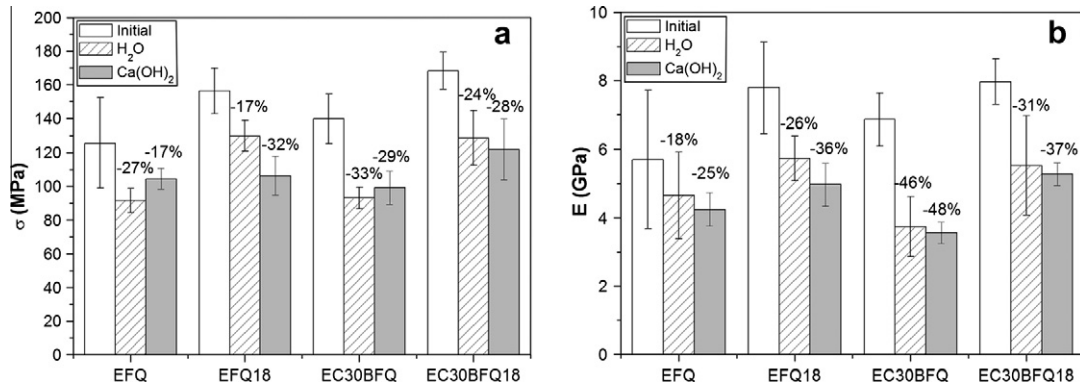


Fig. 13. Flexural properties loss of composites after ageing in water and calcium hydroxide (a) Flexural strength loss (b) Flexural modulus loss.

Table 4  
Percentage of weight gained for composites after inclusion in cement mortar.

Composite	Absorption (%)
EFQ	26.11 ± 0.06
EC30BFQ	6.72 ± 0.01
EC30BFQ18	3.75 ± 0.01

and untreated fibers reduced the absorption by around 4 times respect to the composites with unmodified matrix and untreated fibers. In addition composite with modified matrix and treated fiber reduced their absorption by around 6 times respect to composites with unmodified matrix and untreated fibers.

Fig. 14 shows that composites flexural properties decreased due to the alkaline environment generated in cement mortar. However the effect of mortar in flexural properties loss was less than the effect of water or calcium hydroxide. Since in cement mortar the pH increases over time because calcium hydroxide is a product of hydration in cement curing reaction. Additionally the composite competes with cement for the water because cement requires water during its curing reaction.

The results of flexural strength loss of composite included in mortar are in agreement with reported above for composites in water or calcium hydroxide. The presence of voids in the matrix favored the de flexural strength loss, since composites with modified matrix gets reduced its flexural strength in greater proportion respect to the composite with unmodified matrix. However the flexural modulus was less affected in composites with lower absorption.

Table 5  
Mechanical properties of epoxy-fique composites and construction conventional woods.

Specimen	Flexural modulus (GPa)	Flexural strength (MPa)
OSB [1]	5	490–810
<i>Pinus Elliottii</i> [37]	6	78
<i>Pino Parana (Araucaria angustifolia)</i> [37]	12	133
<i>Eucalyptus grandis</i> [37]	9.6	72
Bamboo [38]	7–12	80–125
EFQ18	7.8 ± 1.3	156 ± 13
EFQ18/H <sub>2</sub> O	5.7 ± 0.6	130 ± 9
EFQ18/Ca(OH) <sub>2</sub>	5.0 ± 0.6	106 ± 11
E30BFQ18	8.0 ± 0.7	168 ± 11
E30BFQ18/H <sub>2</sub> O	5.5 ± 1.4	128 ± 16
E30BFQ18/Ca(OH) <sub>2</sub>	5.0 ± 0.3	122 ± 18

4.7. Comparison to properties of epoxy fique composites with conventional materials used in construction

Of the several materials used in construction, NFCs have properties most similar to wood, bamboo and oriented strandboard (OSB). Table 5 presents a comparison between flexural properties of conventional wood used in Latin-Americans construction and composites with better mechanical properties before and after ageing (EFQ18, EC30BFQ18). Epoxy fique composites before and after ageing have flexural strengths comparable to bamboo and *araucaria angustifolia* and around 2 times higher than *pinus eliottti*, *eucalyptus grandis*; while flexural strength of composites is lower than flexural strength of OSB. Moreover the flexural modulus of composites with unmodified matrix is higher than flexural modulus of OSB and

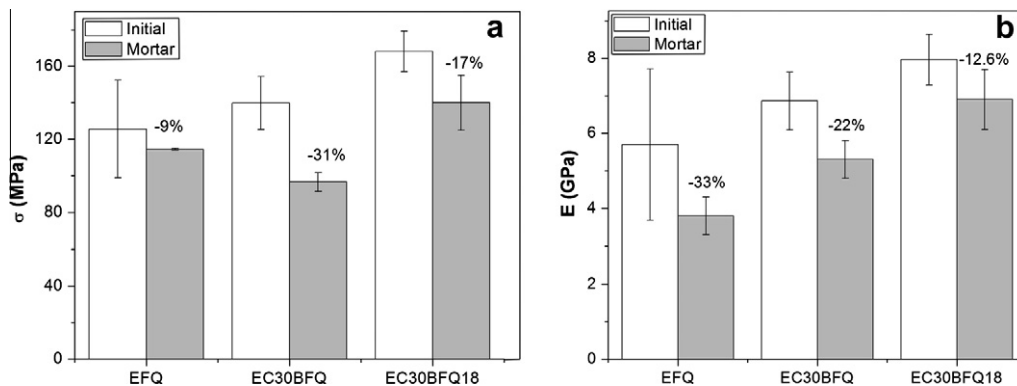


Fig. 14. Flexural properties loss of composites after ageing in cement mortar environment (a) Flexural strength loss (b) Flexural modulus loss.

pinus eliottii. Furthermore the flexural modulus of composites with unmodified matrix is comparable to araucaria angustifolia, eucalyptus grandis and bamboo.

## 5. Conclusions

Physical and mechanical properties of fique composites for construction application were evaluated. It was found that composites decreased their flexural properties after 20 days submitted to three types of environments: composites in distilled water (pH = 6.0); composites in alkaline solution (pH = 12.0), and composites included in cement mortar, cured in a lime stone saturated solution.

The flexural properties of composites increased more after fibers treatment than after matrix modification. Since alkaline treatment improved the interface between fibers and matrix, while modification of matrix with montmorillonite C30B incorporated voids into the matrix.

Improvements at the interface of composites also reduced the water and calcium hydroxide absorption by 6 times. Composites with treated fiber reached the lowest diffusion coefficient value while the modification of matrix with montmorillonite C30B created a tortuous path for water and calcium hydroxide.

The flexural properties loss depends on the absorption medium: water, calcium hydroxide or mortar. The flexural modulus for all composites decreased more after exposition to calcium hydroxide than after exposition to water. On the other hand, the flexural strength gets reduced to greater proportion for the composites immersed in water than for the composites immersed in calcium hydroxide except for composites with treated fibers, they behave in opposite way. Since treated fibers were affected to a greater proportion for the dissolution of the cellulose and the remaining hemicellulose and lignin than untreated fibers. The flexural strength loss for composites included in mortar are in agreement with reported above for composites in water or calcium hydroxide. The presence of voids in the matrix favored the flexural strength loss. However in mortar the flexural modulus was less affected in composites with lower absorption.

The mechanical properties of composites were compared to conventional wood used in construction. The properties of epoxy composites resulted comparable to or higher than properties reported for wood with exception of the flexural strength of OSB. The flexural modulus of epoxy fique composites was better than modulus of OSB and comparable to after composites ageing. This comparison suggests that epoxy fique composites should be able to substitute or replace conventional wood used in construction.

## Acknowledgements

The authors acknowledged to CONICET and to the Agencia de Promoción Científica y Tecnológica (ANPCyT) from the Ministerio de Ciencia, Tecnología e Innovación Productiva de Argentina (Project PICT 08-0223).

## References

- Christian SJ, Billington SL. Mechanical response of PHB- and cellulose acetate natural fiber-reinforced composites for construction applications. *Compos Part B Eng* 2011;42(7):1920–8.
- Dweib MA, Hu B, O'Donnell A, Shenton HW, Wool RP. All natural composite sandwich beams for structural applications. *Compos Struct* 2004;63(2):147–57.
- Van Wyk L. The application of natural fibre composites in construction: a research case study. In: Sixth international conference on composite science and technology, ICCST/6. Durban South Africa; January 2007. p. 1–14.
- Singh B, Gupta M. Performance of pultruded jute fibre reinforced phenolic composites as building materials for door frame. *J Polym Environ* 2005;13(2):127–37.
- Ramakrishna G, Sundarajan T. Impact strength of a few natural fibre reinforced cement mortar slabs: a comparative study. *Cement Concr Compos* 2005;27(5):575–82.
- Kriker A, Bali A, Debicki G, Bouziane M, Chabannet M. Durability of date palm fibres and their use as reinforcement in hot dry climates. *Cement Concr Compos* 2008;30(7):639–48.
- Singh B, Gupta M. Natural fiber composites for building application. In: Mohanty AK, Misra M, Drzal LT, editors. *Natural fibers, biopolymers, and biobased composites*. Boca Raton (FL): CRC Press, Taylor & Francis Group; 2005. p. 261–90.
- Kajorncheappunngam S, Gupta RK, GangaRao HVS. Effect of aging environment on degradation of glass-reinforced epoxy. *J Compos Constr* 2002;6(1):61–70.
- Purnell P, Beddows J. Durability and simulated ageing of new matrix glass fibre reinforced concrete. *Cement Concr Compos* 2005;27(10):875–84.
- Jhon MJ, Francis B, Varughese KT, Thomas S. Effect of chemical modification on properties of hybrid fiber biocomposites. *Compos Part A: Appl Sci Manuf* 2008;39(2):352–63.
- Ray D, Sarkar BK. Characterization of alkali-treated jute fibers for physical and mechanical properties. *J Appl Polym Sci* 2000;80(7):1013–20.
- Alvarez VA, Ruseckaite RA, Vazquez A. Mechanical properties and water absorption behavior of composites made from a biodegradable matrix and alkaline-treated sisal fibers. *J Compos Mater* 2003;37(17):1575–88.
- Yasmin A, Luo JJ, Abot JL, Daniel IM. Mechanical and thermal behavior of clay/epoxy nanocomposites. *Compos Sci Technol* 2006;66(14):2415–22.
- Qi B, Zhang QX, Bannister M, Mai YW. Investigation of the mechanical properties of DGEBA-based epoxy resin with nanoclay additives. *Compos Struct* 2006;75(1–4):514–9.
- Liu W, Mohanty AK, Drzal LT, Askel P, Misra M. Effects of alkali treatment on the structure, morphology and thermal properties of native grass fibers as reinforcements for polymer matrix composites. *J Mater Sci* 2004;39(3):1051–4.
- Shina E, Rout SK. Influence of fiber surface treatment on structural thermal and mechanical properties of jute fiber and its composite. *Bull Mater Sci* 2009;32(1):65–75.
- Zuluaga R, Pataux J-L, Cruz J, Velez J, Mondragon I, Gañán P. Cellulose microfibrils from banana farming residues: isolation and characterization. *Carbohydr Polym* 2009;76(6):51–9.
- Sgriccia N, Hawley MC, Misra M. Characterization of natural fiber surfaces and natural fiber composites. *Compos Part A: Appl Sci Manuf* 2008;39(10):1632–7.
- Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 2007;86(12–13):1781–8.
- Kostic M, Pejic B, Skundric P. Quality of chemically modified hemp fibers. *Bioresour Technol* 2008;99(1):94–9.
- George J, Janardhan R, Anand JS, Bhagawan SS, Thomas S. Melt rheological behaviour of short pineapple fibre reinforced low density polyethylene composites. *Polymer* 1996;37(24):5421–31.
- Valadez-Gonzalez A, Cervantes-Uc JM, Olayo R, Herrera-Franco PJ. Effect of fiber surface treatment on the fiber-matrix bond strength of natural fiber reinforced composites. *Compos Part B Eng* 1999;30(3):309–20.
- Mylsamy K, Rajendran I. The mechanical properties, deformation and thermomechanical properties of alkali treated and untreated Agave continuous fibre reinforced epoxy composites. *Mater Des* 2011;32(5):3076–84.
- Rong MZ, Zhang MQ, Liu Y, Yang GC, Zeng HM. The effect of fiber treatments on the mechanical properties of unidirectional sisal-reinforced epoxy composites. *Compos Sci Technol* 2001;61(10):1437–47.
- Goda K, Sreekala MS, Gomes A, Kaji T, Ohgi J. Improvement of plant based natural fibres for toughening green composites – effect of load application during mercerization of ramie fibres. *Compos Part A: Appl Sci Manuf* 2006;37(12):2213–20.
- Manfredi LB, De Santis H, Vazquez A. Influence of the addition of montmorillonite to the matrix of unidirectional glass fibre/epoxy composites on their mechanical and water absorption properties. *Compos Part A: Appl Sci Manuf* 2008;39(11):1726–31.
- Liu YP, Hu H. X-ray diffraction study of bamboo fibers treated with NaOH. *Fibers Polym* 2008;9(6):735–9.
- Fengel D, Wegener G, editors. *Wood chemistry ultrastructure reactions*. Germany: Verlag Kessel; 2003.
- Peršin Z, Stana-Kleinschek K, Sfligoj-Smole M, Kreže T, Ribitsch V. Determining the surface free energy of cellulose materials with the powder contact angle method. *Text Res J* 2004;74(1):55–62.
- Stana-Kleinschek K, Ribitsch V, Kreže T, Sfligoj-Smole M, Peršin Z. Correlation of regenerated cellulose fibers morphology and surface free energy components. *Lenzinger Berichte* 2003;82(1):83–95.
- Chin JW, Nguyen T, Aouadi K. Sorption and diffusion of water, salt water, and concrete pore solution in composites matrices. *J Appl Polym Sci* 1999;71(3):483–92.
- Pejic BM, Kostic MM, Skundric PD, Praskalo JZ. The effects of hemicelluloses and lignin removal on water uptake behavior of hemp fibers. *Bioresour Technol* 2008;99(15):7152–9.
- Espert A, Vilaplana F, Karlsson S. Comparison of water absorption in natural cellulosic fibers from wood and one-year crops in polypropylene composites and its influence on their mechanical properties. *Compos Part A: Appl Sci Manuf* 2004;35(11):1267–76.

- [34] Mazuki AAM, Akil HM, Safiee S, Ishak ZAM. Degradation of dynamic mechanical properties of pultruded kenaf fiber reinforced composites after immersion in various solutions. *Compos Part B Eng* 2011;42(1):71–6.
- [35] Joseph PV, Rabello MS, Mattoso LHC, Joseph K, Thomas S. Environmental effects on the degradation behaviour of sisal fibre reinforced polypropylene composites. *Compos Sci Technol* 2002;62(10–11):1357–72.
- [36] Maggana C, Pissis P. Water sorption and diffusion studies in an epoxy resin system. *J Polym Sci, Part B. Polym Phys* 1999;37(11):1165–82.
- [37] Instituto Nacional de Tecnología Industrial CITEMA INTI. Pinos-propiedades mecánicas y físicas. <<http://www.inti.gov.ar/maderas/pdf/pinos.pdf>>. [11.08.11].
- [38] Ghavami K. Ultimate load behaviour of bamboo-reinforced lightweight concrete beam. *Cement Concr Compos* 1995;17(4):281–8.