Cellulosic fiber reinforced cement-based composites: a review of recent research

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Abstract

In the last few years, an increase in interest has been given to the use of cellulose fibers as alternatives for conventional reinforcements in composites. The development of commercially viable environmentally friendly and healthy materials based on natural resources is on the rise. In this sense, cellulosic fibers as reinforcements for cement mortar composites constitute a very interesting option for the construction industry.

This paper presents a review of the research done during the last years in the area of the cement-based composites reinforced with cellulose fibers. The fibers used, processing methods, mechanical behavior and durability are presented. The main achievements found have been the development of durable cement composites with optimized fiber-matrix adhesion. Moreover, the recently developed textile composites will allow obtaining high performance materials reinforced with vegetable fibers.

Keywords*:* *cellulosic fibers, cement-based composites, composite processing, mechanical properties, durability*

1. Introduction: the role of cellulosic fibers as reinforcement in cement matrices

Over the last few years, problems related to environmental issues have motivated extensive research on environmentally friendly materials. Particular interest has been given to the use of fibers obtained from renewable vegetable sources in composite materials [1-4]. A combination of interesting mechanical and physical properties and their environmental benefits has been the main driver for their use as alternatives for conventional reinforcements.

Vegetable or cellulose fibers (VF) exhibit a set of important advantages, such as wide availability at relatively low cost, bio-renewability, ability to be recycled, biodegradability, non-hazardous nature, zero carbon footprint, and interesting physical and mechanical properties (low density and well-balanced stiffness, toughness and strength) [5-6]. Vegetable fibers can be found in a wide variety of morphologies – diameter, aspect ratio, length, and surface roughness – and form – mainly strands, pulp or staple. Moreover, their surface can be easily modified in order to have a more hydrophilic or hydrophobic character or to attach functional groups [4].

Although brittle building materials have been reinforced with vegetable fibers since ancient times, the concept of VF reinforcement in cement-based materials was developed in 1940s, when these fibers were evaluated as potential substitutes for asbestos fibers [7]. Since then, considerable effort has been made toward the application of VF as a reinforcing material for the production of building components at low cost. Nowadays, the need for sustainable, energy efficient construction materials has oriented extensive research on alternative materials to produce environmentally friendly construction products. Applications of VF cement composites are basically addressed to the non-structural building of thin walled materials, mainly thin-sheet products for partitions, building envelope or ceilings flat sheets, roofing tiles and pre-manufactured components in general [8].

VF cement composites exhibit improved toughness, ductility, flexural capacity and crack resistance compared with non-fiber-reinforced cement-based materials. The major advantage of fiber reinforcement is the behavior of the composite after cracking has started, as the fibers bridge the matrix cracks and transfer the loads. The post cracking toughness may allow more intensive use of such composites in building. Cellulosic fibers provide adequate stiffness, strength and bonding capacity to cement-based matrices for substantial enhancement of their flexural strength, toughness and impact resistance [9-11]. Moreover, these fibers can reduce the free plastic shrinkage [12]; decrease the thermal conductivity [13] and improve the acoustic performance increasing the sound absorption and the specific damping and the density of the composite [14]

Despite all the aforementioned advantages, the industrial production of cement-based composites reinforced with VF is currently limited by the long-term durability of these materials. The durability problem is associated with an increase in fiber fracture and a decrease in fiber pull-out due to a combination of the weakening of the fibers by alkali attack, fiber mineralization due to the migration of hydration products to lumens, and space and volume variation due to their high water absorption [15-18]. This causes the material to have a reduction in post-cracking strength and toughness.

The role of cellulosic fibers as reinforcement lies in combining in an adequate manner the proper interfacial bond between the fiber and the matrix as well as to ensure the durability of the material.

In this paper we present a review of the research done during the last years (2000-2013) in the area of the cement-based composites reinforced with cellulose fibers. The fibers used, processing methods, mechanical behavior and durability are presented.

2. Cellulose fibers used as reinforcement in cement-based composites

Vegetable or cellulose fibers are mainly composed of cellulose, with varying amounts of lignin and hemicelluloses and other minority components, such as water, proteins, peptides and inorganic compounds. All vascular plants which can be found in nature can be used as sources of cellulosic fibers. However, the use of a particular plant as a source of fiber for a given application will depend on their availability and cost of extraction [19].

According to their origin and composition, cellulosic fibers are classified as non-wood and wood fibers . Wood fibers are also known as lignocellulosic fibers because they have a higher lignin content than non-wood fibers. The non-wood fibers can be classified into four main groups: depending on the part of the plant used to extract the fibers: bast fibers (hemp, jute, kenaf, flax, ramie and others), leaf fibers (sisal, henequen, pineapple, oil palm leaf fibers, banana, and others), stalk fibers (straws –as rice, wheat and barley-; reeds –as bamboo- and grass –as esparto and elephant grass) and seed fibers (cotton, coir, and others) [2,20].

Wood fibers are grouped depending on their origin, into softwood fibers (obtained from pines, firs, etc.) and hardwood fibers (from the birch tree, eucalyptus, beech, etc.) [19].

Apart from its origin, the reinforcements based on cellulose fibers can be classified by the function of their form. Thus, cellulose fibers can be found as strands (long fibers with lengths between around 20 and 100 cm), staple fibers (short length fibers which can be spun into yarns), or pulp (very short fibers of lengths around 1 to 10 mm which should be dispersed into water to separate them) (Figure 2).

Figure 1. Images of vegetable fibers in different forms: (a) strands, (b) staple, (c) pulp.

The strands or staple fibers are obtained from crop or wild plants directly from the plants or after a water retting process. In this group are included cellulose fibers traditionally used by the textile industry which are characterized by its high aspect ratio and low linear mass.

The pulps are generally obtained from wood sources by a pulping process Depending on the treatment used to destroy or weaken the inter-fiber bonds the pulping processes can be mechanical, thermal, chemical or some combination of these treatments. Pulps can also be obtained from non-wood sources [19].

The physical-chemical properties of the vegetable fibers often depend on the sources, cultivation and harvesting methods and processing, as well as its form.

Composites reinforced with fibers are usually classified as *Fiber Reinforced Composites* (FRC), which contain short fibers – staple or pulp – randomly dispersed into the matrix, and *Textile Reinforced Composites* (TRC) which contain fibers in the form of aligned strands or textile structures, also known as structural composites. The reinforcement capacity of FRC depends on the type of reinforcement and the amount of fiber used, its geometry (length/thickness ratio), and its distribution and adhesion to the matrix. In TRC the reinforcing ability depends also on the textile structure used. The textile structures commonly used for reinforcing composites are nonwoven fabrics or fiber mats – in which the fibers are randomly distributed – woven fabrics or multidirectional fabrics.

As can be seen in Table 1, a wide variety of fibers from different forms and origins have been used to reinforce cementitious matrices. As shown, pulp is the most common fiber form. This is because cellulose pulps are a cheap raw material – used generally by the paper industry – and can be easily dispersed in water, a basic component for the preparation of cementitious materials. The majority of cellulosic pulps used to reinforce cement-based materials are provided from wood resources and are obtained chemically (kraft pulp). For instance, experienced researchers in cement composites, such as Savastano and co-workers have successfully used pinus pulp [8, 21-23] and eucalyptus pulp [8][21][23][25-29] with percentages in the range of 4–10 wt% to reinforced Portland cement matrices. Mohr and co-workers have also worked with pinus pulp obtained from chemical and thermo-mechanical treatments with percentages around 4 wt%.

Another important source of pulp fibers used to reinforce composites is sisal [9][11][18][21][22][27][30-32]. Sisal is a crop plant which is a very abundant and cheap source of fibers. Pulps from banana [21][26][27][30], fique[7][33], cotton linters [34] and agricultural waste [35] have been also successfully used to prepare cement-based composites.

Apart from short fibers in the form of pulp, other studies reported the preparation and characterization of cementitious composites with coir fibers [11][12][33][38], malva [36], jute, or hemp in staple or flock form [37].

The physical properties of the main pulps used are presented on Table 2. As can be seen, their properties depend not only on the fiber source also on the pulping process used to obtain the fibers. In general terms the mechanical behaviour of the composite will depend on the fibre type, length, diameter, aspect ratio and texture of the fibres [35]. The use of pulped fibres facilitates two-dimensional and homogeneous distribution of the fibres in the cementitious matrix. It is because this, the use of pulp in comparison to use of short of flock fibres form results in better fibre-matrix bond an greater reinforcing efficiency [39].

Finally, only a few works use continuous reinforcement in the form of fiber strands. As far as we know, the only reported work with long fibers have been made by Toledo Filho and co-workers [40-46]. In this case it is possible to perform a structural reinforcement and the mechanical properties of the composite are considerable improved.

Table 1. Cellulose fibers used as reinforcement for cement composites

Fiber source	Fiber form	wt%	Reference
Softwood (pinus)	Pulp (chemical-kraft) Pulp (thermo-mechanical) Paper sheets Pulp (chemical-kraft) from waste	4–12 10 1,2,3,5 4 1,3 1–14 5,10,15 8 0–7 4 1, 3 3.5, 8 2.5 2–16 ---	[22][21] [23] [25] [24] [8] [47] [16] [48][17] [49] [50] [51] [52] [14] [34] [49] [10] [53] [13]] [54][55][56]
Hardwood (eucalyptus)	Pulp (chemical-kraft)	8 10 5 1,2,3,5 2–4	[30] [21] [26] [27] [23] [25] [41] [29] [8] [35]
Crop plant (bast fiber): jute	Strands (13-152 cm)	---	[37]
Crop plant (bast fiber): hemp	Strands (13-152 cm)	---	[37]
Crop plant (leaf fiber): sisal	Pulp (kraft) Staple Strands (18-60 cm)	4–12 4 -- 3 (v.) 10 (v.)	[22] [30] [31][9] [32] [21] [26] [27] [9] [21] [37] [18] [57] [12] [42] [44] [45] [40] [43] [41] [46]
Crop plant (leaf fiber): Malva	Staple	4 (v)	[36]
Crop plant (leaf fiber): banana	Pulp (chemical-kraft)	8 4	[30] [21][26][27]
Crop plant (leaf fiber): Agave lechuguilla	staple	---	[58]
Crop plant (leaf fiber): fique	Pulp	3 2.5	[7] [33]
Crop plant (seed fiber): coir	Staple Mesh Pulp	4 (v.) 3 (v.) --- 2.5	[36] [37] [11][12] [11] [33]
Crop plant (seed fiber): cotton linters	pulp	4	[34]
Agricultural waste: sugar cane stalk	Pulp (mechanical)	2–4	[35]
Agricultural waste: wheat straw	Pulp (mechanical)	2–4	[35]

Table 2. Physical properties of the pulps used to reinforce cement based composites

Fiber type	Process	Length (mm)	Width (µm)	Aspect ratio	Reference
Sisal	Thermo-mechanical	2.25	10.2	221	[9]
Sisal	Chemical-thermomechanical	2.46	12.7	194	[9]
Sisal (by-product)	Chemical-thermomechanical	1.61	10.9	148	[9]
Sisal	Kraft	1.65	13.5	122	[30]
Sisal	Kraft	1.66	22.2	75	[32]
Sisal	Kraft +beating	1.13	18.7	60	[32]
Sisal	Kraft + geating	0.79	20	40	[32]
Pine	Bleached kraft (surface treated)	2.94	31.4	94	[10]
Pine	Kraft	3.05	32.4	94	[10]
Pine	Kraft	2.7	29.3	92	[10]
Pine	Kraft	2.73	32.5	84	[10]
Pine	Kraft	2.97	34.1	87	[10]
Pine	Kraft	2.70	30.7	88	[10]
Pine	Kraft	2.93	32.6	90	[10]
Pine	Chemical-thermomechanical	1.71	32.4	53	[21]
Pine	Kraft	1.37	28	49	[34]
Banana	Kraft	1.95	15.3	127	[30]
Banana	Chemical-thermomechanical	1.99	20.1	99	[27]
Cotton linters	Thermo-mechanical	0.79	20	40	[34]
Eucalyptus		0.83	16.4	51	[28]
Eucalyptus	Kraft	0.66	10.9	61	[30]
Eucalyptus	Pulping waste	1.12	480	2	[35]
Bagasse	Pulping waste	1.303	348	4	[35]
Wheat	Pulping waste	1.238	345	4	[35]

3. Processing

The final properties of cellulose fiber cement composites depend, aside from the fiber and the matrix components, on the manufacturing process. The main goals to achieve in order to develop composites with well-balanced mechanical properties are the following:

1) A homogeneous dispersion of the fibers in the matrix;

2) A well-balanced interaction between the cement matrix and the fibers to allow fiber pull-out;

2) A low porosity of the matrix;

3) An optimized percentage of fibers: enough to reinforce the material while allowing a continuity of the matrix.

The majority of the fabrication methods for cement composites reinforced with cellulose fibers in the pulp form are based on the Hatschek process, patented by L. Hatschek in 1900. It is a semi-continuous process comprised of three steps: sheet formation, board formation, and curing. In the first step, a conveyor belt is soaked in a mixture of fresh fiber cement supplied by a roller from a tank under continuous agitation. Using a vacuum system, a significant portion of the mixing water is removed from the slurry, forming a very thin sheet (about 1 mm). The board formation is made in a large cylinder which receives the sheet from the previous step and rolls up in successive layers until the required thickness is achieved. Following this, a guillotine cuts the boards and deposites them on a press to compress and mold the board to the desired shape. Finally, the boards are cured under air or steam conditions -autoclave- (Figure 2). These processes produce composites with an adequate percentage of fibers well dispersed into the matrix.

The procedures for preparing cellulose cement composites reported in literature can be divided into two main groups, depending on the fiber form: fibers randomly dispersed in the matrix, and aligned fibers or fibrous structures.

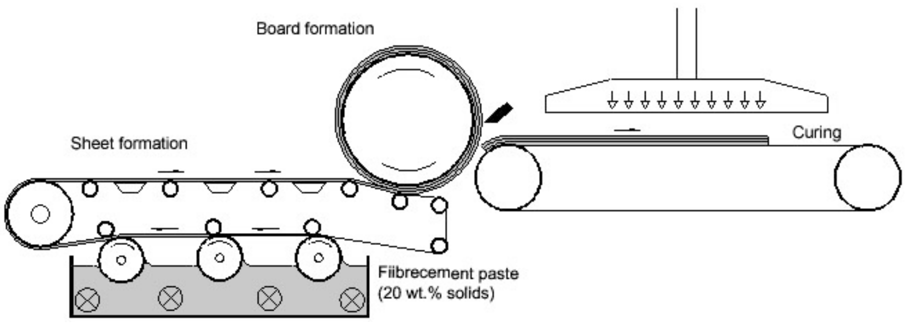


Figure 2. Scheme of the Hatschek process.

3.1. Composites reinforced by fibers randomly dispersed in the matrix

Coutts and Savastano and co-workers [7][9][21-25][28-31] successfully used a variation of the Hatschek process (the slurry vacuum de-watering technique) to prepare cement composites with pulp fiber mass fractions of around 8 wt% (approximately 10% by volume content). In this technique the matrix materials are stirred, with the appropriate amount of fiber dispersed in water, to form a slurry with approximately 20% solid materials. Then the slurry is transferred to a drilled mold and a vacuum is applied as can be seen in Figure 3. Afterward, the board is pressed until it has a thickness up to 15 mm. A similar procedure was also used by Soroushian et al. [52].

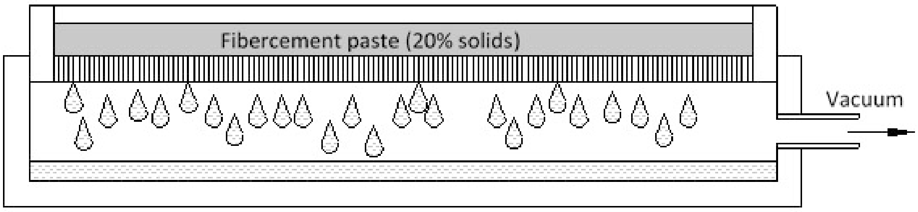


Figure 3. Scheme of the Savastano and co-workers process.

Another possibility based on de-watering with pressure was used to successfully prepare cellulose composites incorporating until 4 wt% of cotton and pinus pulp [34]. The cement paste consists of a mixture of cement, sand, water and fluidizer with a water/cement ratio around 1:1. The cellulose fibers are dispersed in water and incorporated in the paste beforehand. The specimens are prepared in a micro-grilled mold to allow the evacuation of water with a minimum loss of cement and sand. The mold is placed on a plate, then compacted on a vibrating table, and pressed for 24 h to reach a final pressure of 4 MPa (Figure 4).

Figure 4. Mold and press system used to prepare the specimens (from left to right: the molds, vibrating table, pressing system and demolding).

Mohr and co-workers [16-17] [47-49] also successfully prepared cement mortar composites without pressuring or a vacuum using a cast-in-place mix methodology with a 4% fiber volume fraction. In this methodology the pastes are prepared by firstly mixing the pulp fiber with water (approximately 50% water) and superplasticizer. Subsequently, cement is added, and mixing continues to allow uniform fiber dispersion. In some cases, to improve the dispersion of the fibers these were treated by a process with cationic starch and fly ash.

Toledo Filho and co-workers [11-12] [18] also used the casting methodology to prepare cement reinforced composites with short sisal and coconut fibers. In this case, after casting, a conventional vibration table is used.

Finally, Soroushian et al. [51] used the extrusion procedure to prepare cellulose pulp cement composites with up to 8 wt% fibers. These authors used a laboratory-scale de-airing ceramic extruder which allowed the production of flat specimens with 60 mm width and 8 mm thickness. This process allows the alignment of the fibers in the extruder direction generating higher reinforcement capacity.

3.2. Composites Reinforced by aligned fibers or fibrous structures

Other authors, taking into account the limitations of the reinforcement capacity of the pulp or short fibers randomly dispersed in the matrix, have been developing other manufacturing processes for semi-finished products, such as aligned fibers, sheets or nonwovens, which can allow a higher level of enforcement under flexural or tensile work.

In this sense, Toledo Filho and co-workers [40-46] have successfully prepared high-performance cement composites reinforced with aligned sisal strands with the following methodology: firstly the long fibers are cut to the size of the molds, weighed and separated into different layers, resulting in a total volume fraction of 10%. The fibers are stitched to make homogeneous spacing between the fibers and to facilitate the molding process. Then, laminates are produced by placing the mortar mix into the mold one layer at a time, followed by single layers of long unidirectional aligned fibers (up to 5 layers). The samples are consolidated using a vibrating table and, after casting, compressed at 3 MPa for 5 min.

Cement composites reinforced with pulp fibers in the form of aligned perforated sheets were prepared by Mohr et al. [53]. To prepare the composites, firstly a mixture of cement, sand and water is added to the mold and vibrated to level the mortar surface.

Afterwards, the fiber sheet is placed in the mold and lightly tamped to remove trapped air voids beneath the fiber sheet. Finally the remaining mortar is slowly added to the mold, taking care to keep the fiber sheet plane. For the samples with multiple fiber sheet addition, a thin layer of mortar is spread between the fiber sheets to ensure bonding between the sheets.

4. Mechanical behavior

4.1. Composites reinforced with pulp fibers

The vast majority of work dedicated to the study of the mechanical behavior of cement composites with short or pulp cellulose fibers randomly dispersed in the matrix analyze their flexural properties using both the three-point and four-point bending configurations. For this kind of material, thin sections that meet the proportions which allow the development of bending mechanisms are preferably used. The standard TFR1 of RILEM recommends a proportion between the maximum distance between supports and the thickness of the specimen higher than 20 [59]. As this ratio decreases, the compression crank mechanisms in the transmission of the load to the supports increases, distorting the results. This standard establishes the four point bending configuration as the only usable configuration. This configuration allows the part of the specimen between the two loads to be subjected to a pure bending constant effort and the points of the load application to stay away from the break point of the piece, ensuring the correct results are obtained. On the other hand, under the three point bending configuration, the only point subjected to pure bending is the point just under the load application. Moreover, the load generates a squashing on the surface of the specimen near or in the breaking cross section, masking the flexural tests results. Nonetheless, the standard ISO 8336 test establishes that the three point bending configuration can be used to determine the modulus of rupture (MOR) using a proportion between the maximum distance between supports and the thickness of the specimen higher than 15.

The main parameters determined from the force/stress versus displacement/deformation curves to characterize the mechanical behavior of the cement composite materials are (Figure 5): the limit of proportionality stress (LOP), the MOR, the modulus of elasticity (MOE), the energy absorption or toughness, and the strain. The LOP is defined as the stress value at the upper point of the linear portion of the curve. The MOR is the maximum stress reached by the material. The MOE is the tangent of the slope angle of the stress versus deflection curve during elastic deformation.

The equations for the calculation of these parameters depend on the bending configuration (three- or four-point), on the distances between supports and its relationship with the position of the forces, and on the thickness of the specimen (see Table 3).

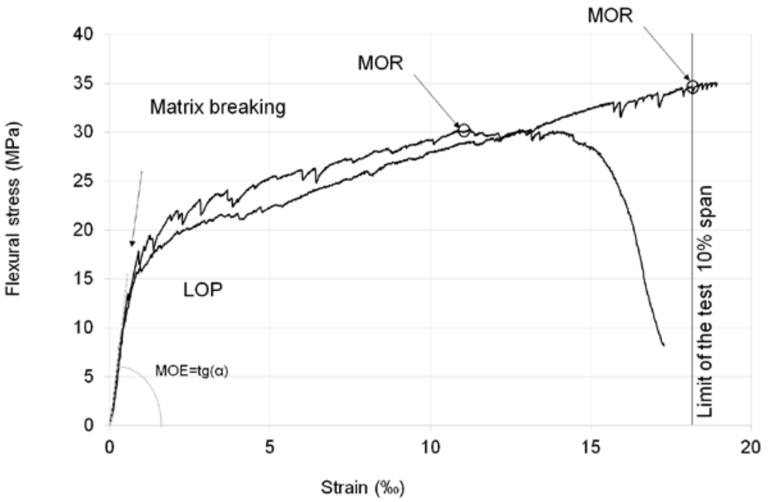
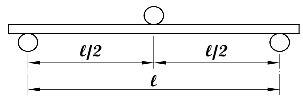
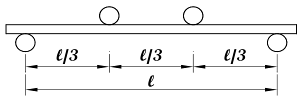
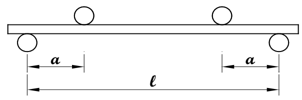


Figure 5. Typical flexural stress-strain curves obtained for cellulose cement composites.

Table 3. Equations for the calculations of the MOR, MOE and strain (δ) for different bending configurations

			
MOR	$\frac{3 \cdot F \cdot l}{2 \cdot b \cdot h^2}$	$\frac{F \cdot l}{b \cdot h^2}$	$\frac{3 \cdot F \cdot a}{b \cdot h^2}$
MOE	$\frac{F \cdot l^3}{4 \cdot f \cdot b \cdot h^3}$	$\frac{23 \cdot F \cdot l^3}{108 \cdot f \cdot b \cdot h^3}$	$\frac{F \cdot a}{4 \cdot f \cdot b \cdot h^2} \cdot (3 \cdot l^2 - 4 \cdot a^2)$
δ)	$\frac{6 \cdot f \cdot h}{l^2}$	$\frac{108 \cdot f \cdot h}{23 \cdot l^2}$	$\frac{12 \cdot f \cdot h}{3 \cdot l^2 - 4 \cdot a^2}$

F = the load (force) (N)
l = length of the support span (mm)
f = maximum deflection (mm)
b = width of the specimen (mm)
h = thickness of the specimen (mm)
a = distance between the support and the position of the load (mm)

Another important parameter for these materials of high ductility is the energy absorbed during the flexural test, defined as the area under the curve force versus displacement from the beginning to the limit of the test. RILEM recommends whichever occurs first to be used as limit: the value of the ordinate corresponding to 40% of MOR value or the deformation value corresponding to 10% of the span [60].

The main drawback of the calculation of this parameter is that the energy is calculated from the force applied to the specimen and from the deformation. These values depend not only on the characteristics of the material but also on the dimensions of the specimen. This makes the comparison between different specimens with different dimensions difficult. To mitigate this problem the toughness parameter has been established, defined as the energy absorbed during the flexural test divided by the cross-sectional area of the specimen [30][40]. Another possibility is to calculate a similar parameter dividing the absorbed energy by the weight of the sample. In any case, the main drawback is the same taking into account that the relationship between the energy absorbed and the cross-sectional area or the weight of the sample is not lineal.

Recently other tests have been developed to obtain more information about the behavior of the composites under temperature and humidity [61], as is shown in Figure 6.

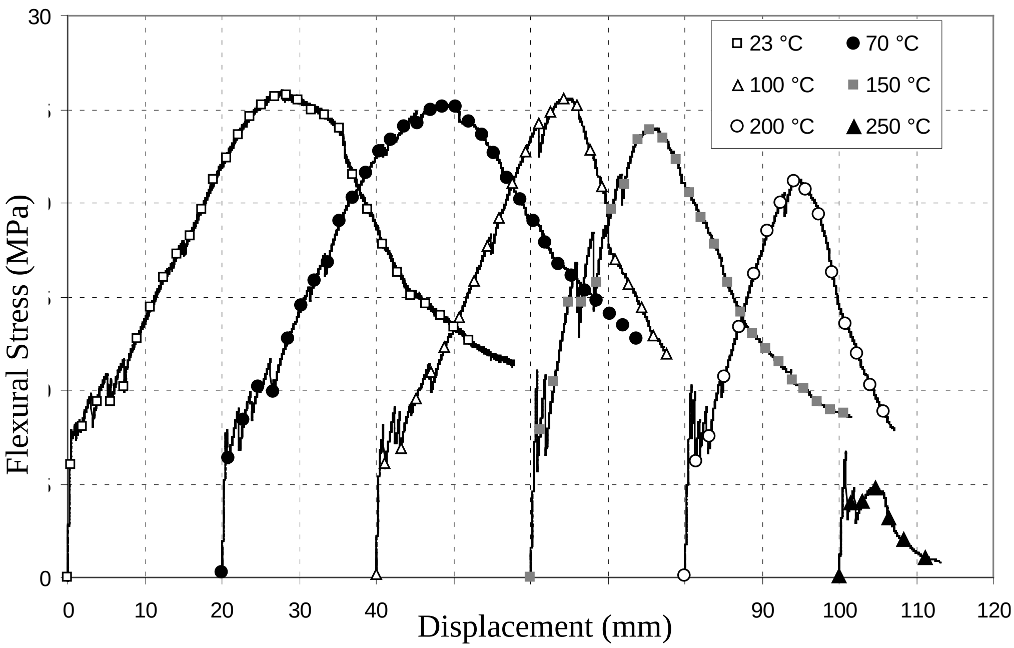


Figure 6. Typical flexural curves obtained for composites subjected to 23°C, 70°C, 100°C, 150°C, 200°C e 250°C.

In general, cellulose-fiber-reinforced composites exhibit curves like the one presented in Figure 5, having higher maximum peak strength and post-cracking toughness that the neat matrix.

Concerning the effect of cellulose fiber type, Savastano et al [22] [26] analyzed the mechanical properties of a ground iron blast furnace slag (BFS) matrix reinforced with pinus and sisal pulps under a three point bending configuration, comparing the results with an ordinary Portland cement matrix (OPC). They found that the mechanical properties of the BFS and OPC matrix types were enhanced in a like manner by 4 and 8 wt% of reinforcement, respectively, of wood or sisal pulps, providing significant incremental improvements in flexural strength. The best performance in terms of flexural strength was for BFS based composites reinforced with wood pulp at fiber loadings between 8 and 12% with values around 24 MPa. The fracture toughness of the composites reinforced with 12 wt% of wood pulp ranged from 1.72 Kj/m^2 to 2.36 KJ/m^2. The fracture toughness values of sisal pulp were lower than those corresponding to wood pulp. The authors explained that the lesser performance of sisal fibers could be a direct consequence of their lower strength and that they have not been beaten in terms of generating external fibrillation and composite packing. These factors would act to reduce the extent of matrix microcracking. The elastic moduli fell continuously with the increase of fiber content and they obtained values in the range of 4.3–6.2 GPa for 12% wood or sisal reinforced BFS composites.

In the same way Claramunt et al. [34] studied the performance of OPC composites reinforced with kraft pinus fibers compared with cotton linters pulp. Despite the tensile tests results obtained for the single fibers being better for the cotton linters (16% higher strength and 37% higher modulus of the cotton linters with respect to the kraft pulp), the composites prepared with the pinus pulp had higher performance. This behavior was explained by the higher ratio of length to diameter of the pinus pulp (19% higher than for the cotton linters).

Another interesting piece of research performed by the research group of Savastano [32] analyzed the effect of sisal pulp with three different degrees of refinement on the mechanical performance of the composites. These authors found that an intermediate refinement degree resulted in significant improvement in the MOR of cement-based composites. However, the excessive refinement caused some decay in mechanical performance. These authors suggested that the better adhesion of the fibers reduced the incidence of fiber pull-out during composite fracture with consequent damage to the toughness of the material. The same authors found similar results for eucalyptus pulp [23]. That is to say, refining significantly increased the MOR but reduced the toughness. A similar trend was found by Ardanuy et al. [62] comparing the effect of conventional with nanofibrillated pulps. For a fixed 4 wt% content, it was found that unlike the composites reinforced with nanofibrillated cellulose, the ones reinforced with conventional pulp had a more pseudo-plastic behavior (Figure 7). These results were explained since long fibers were more effective in bridging the crack faces and the low-fiber specific surface area favored toughening by deboning and fiber pull-out.

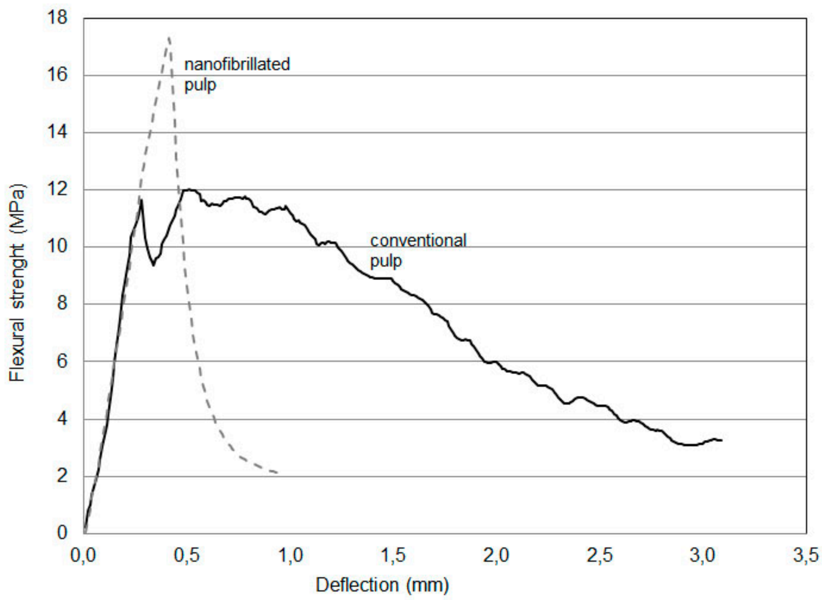


Figure 7. Typical flexural curves of cement composites reinforced with nanofibrillated pulp compared with conventional sisal pulp.

Tonoli et al.[25] studied the effect of the surface modification of eucalyptus fibers on the mechanical performance of cement composites. Two silane types were used to modify the fibers: methacryloxypropyltri-methoxysilane (MPTS) and aminopropyltri-ethoxysilane (APTS). The authors found that the composites reinforced with APTS-modified fibers presented higher flexural strength than those associated with composites made of unmodified and MPTS-modified pulps. They also found that the toughness of the composites was not influenced by modification with silane coupling agents.

A study conducted by Khorami and Ganjian [35] compared the flexural behavior of cement composites reinforced with agricultural waste fibers of bagasse (obtained from sugar cane stalk), wheat and eucalyptus at 2 and 4 wt% loadings in OPC matrices. They found that 2 wt% fiber content led to little change in the flexural behavior of the control specimen. However, increasing the content, 4 wt% changed the flexural behavior considerably. The better performance was found for waste fibers obtained from sugar cane fiber and the result was attributed to the high tensile strength and the high aspect ratio of the bagasse fiber rather compared with the wheat and eucalyptus fibers. The same authors [50] analyzed the effect of the fiber content on the flexural properties of cement composites reinforced by waste kraft pulp fibers in another recent study. They found that the optimum percentage of fiber content for reinforcing cement was about 8 wt%, obtaining a MOR value 2.5 times higher than the control specimens. These authors also reported that, by increasing the amount of kraft fibers, ductility increased. Using a similar approach, Bentchikou et al. [13] analyzed the effect of the content of pulp fibers obtained from waste paper and packaging (between 0 to 16 wt%) in the compressive and flexural strength of cement composites. The authors found that the compressive strength decreased with the fiber content. The authors explained this decrease by the fact that increasing fiber content induces more voids which lightens and weakens the material. On the other hand, flexural strength increased between 0 and 4 wt% (from 6 to 7 MPa) and decreased progressively afterwards. The authors suggested that this behavior could probably be due to the superposition of two potential phenomena: an effect of the fiber related to the non-uniform dispersion in the matrix and a weakening response following a reduction of the cementitous matrix volume proportion.

In the same way, Claramunt et al. [63] reported similar results for cement composites reinforced by softwood kraft pulps, varying the wt% of fibers between 0 and 10 wt%. The typical flexural curves are shown in Figure 8. As can be seen, there is a decrease of the maximum strength of the matrix with the increase of the fiber content until 4 wt%. For higher content, the strength of the matrix is maintained at around the 50% of the maximum achieved. At the same time, there is an increase in the strength of the reinforcement which also tends to stabilize at a similar value or slightly greater than that of the matrix for contents of around 4 wt% of fibers. The MOE decreases linearly with the fiber content, while the toughness of the material increases. The SEM observations showed different failure models depending on the content (Figure 9 and Figure 10). For low contents (<2%), the flexural stress failure of the material is due to the fracture of the fibers, i.e., the fiber-matrix bonding is enough to break the fibers. At medium contents (4–6%), there is a loss of fiber-matrix bonding due to the interference of the nearby of the fibers and the fracture mechanism is by pull-out. In this case, the length to thickness ratio of the fibers plays an important role in increasing the toughness of the material. For higher fiber contents (8–10%) there is no reinforcement and the fiber and matrix roles disappear.

In another study, Savastano et al. [9] found similar results. Composites of sisal pulp or sisal staple reached their maximum flexural strengths of 18-20 MPa at fiber contents of about 8%, with an improvement of at least 58% over that of the neat matrix.

Finally, Soroushian and co-workers [51] studied the effect of fiber nature (recycled, softwood and hardwood pulps) and content (5, 10 and 15 wt%) on cement composites processed by extrusion. They obtained composites with flexural strengths ranging from 10 to 20 MPa and flexural toughness ranging from 50 to 300 Nm. The authors found that increasing softwood fiber content from 5 to 15% increases toughness and that the flexural strength increased slightly as fiber content increases from 5 to 10 wt% and then decreased. With respect to the effect of the nature of the fibers, they found that softwood fibers provided balanced improvements in flexural strength and toughness, and that hardwood fibers (with shorter lengths) were worst but more effective than the recycled fibers. The recycled fibers render less reinforcing effects than both softwood and hardwood fibers.

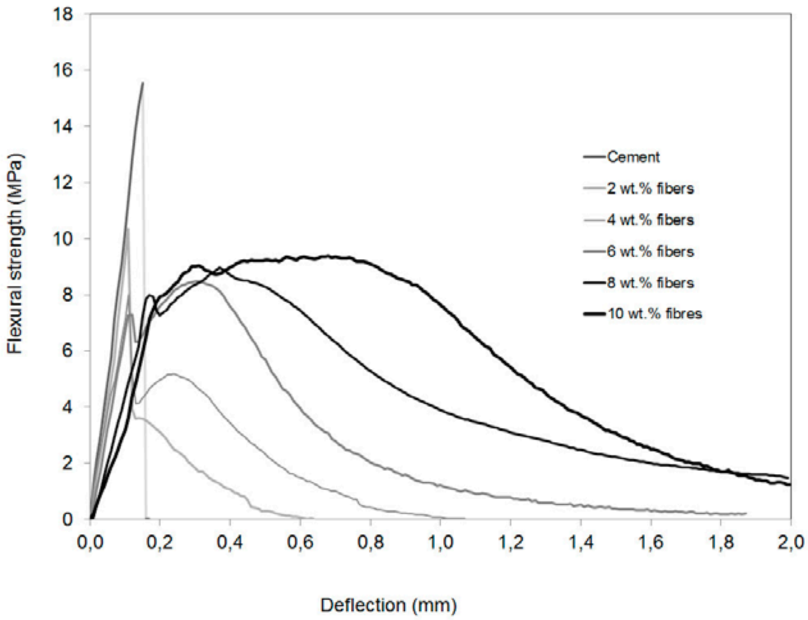


Figure 8. Typical stress-deflection curves of the cement compared with cement mortar composites with various % of pulp fibers.

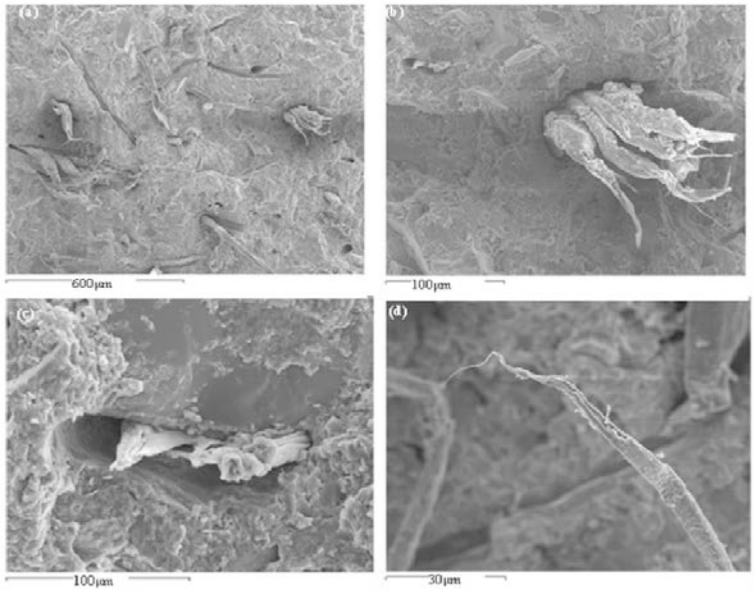


Figure 9. SEM micrographs of cement mortar composites reinforced with 2% wood pulp fibers.

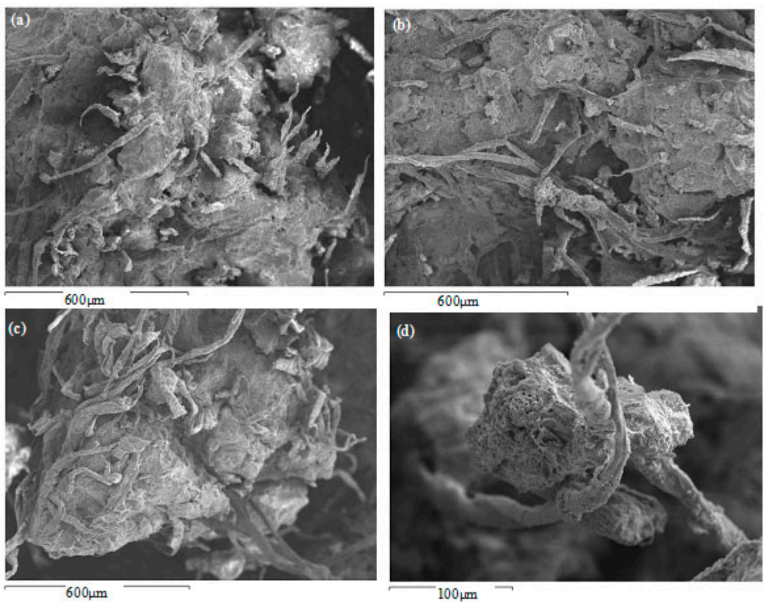


Figure 10. SEM micrographs of cement mortar composites reinforced with 4–6% of wood fibers.

4.2. Reinforced by long fibers and textile structures

As mentioned above, most work on cellulose cement composites are based on short or pulp fibers and, as far as we know, only the research group of Toledo Filho has analyzed the mechanical properties of composites reinforced with long vegetable fibers [42]. In this case they used both tensile tests and the four-point bending test to characterize the materials. They found that the composites showed elastic moduli at linear-elastic zones in the range of 30 GPa under flexural tension and 34 GPa under direct tension. They observed a multiple cracking behavior under both tensile and bending loads. The toughness of the composites was found to be approximately 45 and 22 kJ/m^2 under direct tension and bending loads, respectively. They concluded that sisal fibers were able to bridge and arrest the cracks within the tensile region response, leading to a high mechanical performance and energy absorption capacity. They also studied the fatigue behavior of these composites [40], finding that the composites did not fatigue up to 10^6 cycles when subjected to maximum stress level below 6 MPa (50% of the ultimate tensile strength).

Another possibility to improve the strength and ductility of the composites and make possible the industrial production is the incorporation of long fibers in the form of textile structures, like woven or nonwoven textiles. Recently Claramunt et al. [64-66] have developed new cement based composites reinforced with flax nonwoven reinforcements that have multiple cracking behavior with deflection hardening leading to composites with significant improvement of maximum flexural stress and toughness with respect to the composites reinforced with pulp fibers. Figure 11 shows the typical bending curve of the cement mortar composite reinforced with natural fibre nonwoven compared with the typical one of pulp reinforced composite. As shown, although the LOP and MOE values, related with the behaviour of the matrix, are similar, the MOR and fracture energy increased considerably for the composites reinforced with the nonwoven structures. This is due to the different fracture mechanisms developed depending on the length of the fibers. For long fibers, the higher length and contact with the matrix allow the formation of multiple cracking fracture done when the stress increases. The crack distance is reduced during loading until a steady state condition is reached, and finally there is a progressive damage characterized by a crack widening stage leading to failure by fiber pullout [42]

In similar way, the research group of Toledo Filho used a woven fabric made of jute for reinforcement of concrete finding a high potential of this new material for the development of thin walled elements [67]

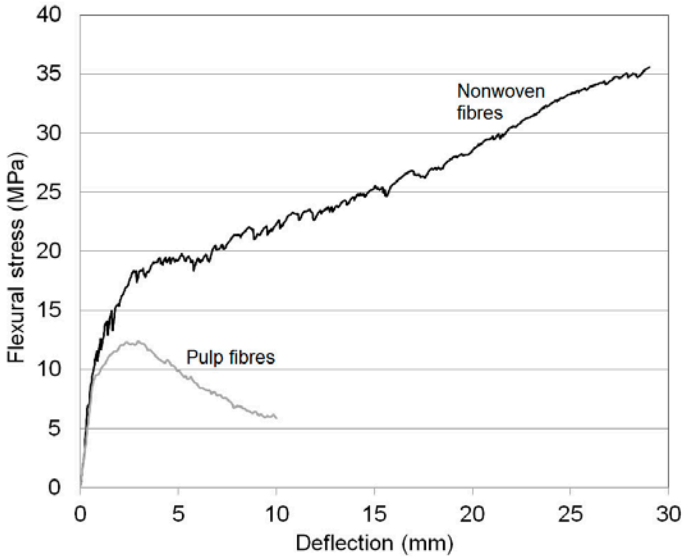


Figure 11. Typical stress versus displacement curve of the nonwoven reinforced composite compared with the typical one of the pulp reinforced composite.

5. Cellulosic Fiber-cement matrix bonding

The mechanical performance of the composites depends not only on the matrix and fiber characteristics, but also on the interface properties. Besides the fiber length, the composite toughness is mainly governed by fiber-matrix bonding. A well-balanced interaction between the cement matrix and the fibers which allows fiber debonding and pull-out as well as the stress transfer from the matrix to the fibers is necessary to obtain cellulose cement composites with high toughness.

Although significant research has been performed to quantitatively determine the bond adhesion of man-made fibers with cement matrices, only a few studies have been focused on vegetable fibers [46] [68].

Silva et al. [46] analyzed the effect of fiber shape and curing age on the bond strength of sisal cement composites using pull-out tests. Concerning the effect of the fiber morphology, they found that the variations of the cross section had significant effects on the bond strength. In this sense, the highest values of bond stress were found for the twisted arch shapes, with an average adhesional and frictional bond strength of 0.92 and 0.42 MPa respectively. With respect to the curing age, the bond strength reached its maximum capacity at 14 days for the matrix studied. In another work, the same research group studied the effect of wet and dry cycles on sisal fiber (hornification) on fiber matrix bonding [69]. They reported an increase of the adhesional and frictional bond strength of 40% and 50% respectively for treated fibers compared with untreated fibers. Moreover, the maximum pull-out load increased with the embedment length, reaching 6.35 and 8.46 N for the untreated and treated fibers, respectively, for a length of 25 mm. The authors attributed this effect to the reduction in dimensional changes due to the hornification process.

Other studies analyzed also the fiber matrix adhesion determining indirectly the fiber matrix bond adhesion [29][70].

6. Methods for improving durability

The main drawback associated with cellulose fibers in cement applications is their durability in the cementitious matrix. As is known, the majority of the cellulose cement composites are based on OPC. This agglomerate hardens by hydration of anhydrous compounds giving rise to calcium silicate hydrate (CSH gel), ettringite and calcium hydroxide or portlandite. Although the stoichiometric water/cement ratio is around 0.23, it becomes necessary to add more water to mix the components. This excess of water evaporates during the curing step leading to porous network cement. This porosity is one of the causes of the lack of durability of the cement pastes, given that it allows the access of water -which can contain different dissolved substances (chloride or sulfate salts or acids among others)- or gases from the outside into the inside of the cement material. Furthermore, depending on climatic conditions, the pore network may be dry, semi-saturated and saturated (in humid weather with >65% relative humidity). Under these conditions, the interstitial water dissolves calcium hydroxide to form a buffered solution of pH>13. Many studies have related the presence of this calcium hydroxide with the degradation of vegetable fibers, and thus with the loss of durability of the cellulose fiber reinforced cement-based composites [7][15-18][57][71]. Mohr et al. [16] established the following sequence of damage which occurs in the vegetable fibers when the composite is subjected to various wet–dry cycles: (a) loss of adherence between the fiber and the matrix after the second wet–dry cycle; (b) reprecipitation of the hydrated compounds within the void space at the former fiber–cement interface during the first ten wet–dry cycles; (c) full mineralization, and thus the embrittlement of the vegetable fibers after ten wet–dry cycles. Likewise, Toledo Filho et al. [18] demonstrated the alkaline attack of the fibers after various wet–dry cycles. They analyzed the durability of sisal and coconut fibers in alkaline media and cement mortar composites. They found sisal and coconut fibers immersed in a high alkaline media of calcium hydroxide for 300 days completely lost their flexibility. They attributed this mainly to the crystallization of lime in the lumen, walls and voids in the fiber. The extent of the alkaline attack was smaller when the fibers were conditioned in a sodium hydroxide solution. The embrittlement was mainly associated with the mineralization of the fibers due to the migration of hydration products, especially calcium hydroxide, to the fiber lumen, walls and voids. They also found that embrittlement of composites manufactured with short sisal fibers was greater than that observed in specimens reinforced with long fibers. The authors attributed this effect to the higher number of end points and larger surface area of the short fibers, which allowed a faster penetration of cement hydration products and consequent mineralization of the fibers.

Using an X-ray diffraction (XRD) technique and Thermogravimetric Analysis (TGA), Claramunt et al. [15][34] corroborated the migration of the hydration compounds of the cement to the vegetable fibers according to the following process: (a) in the first dry cycle the transversal section of the vegetable fibers is reduced due to the loss of water. This reduction causes loss of adherence with the matrix and the appearance of void spaces at the fiber–matrix interface; (b) in the subsequent wet cycle, the water dissolves the hydration compounds of the cement (calcium hydroxide). The vegetable fibers absorb this dissolution of calcium hydroxide and thus swell; (c) in the second dry cycle, water is lost through evaporation and the calcium hydroxide precipitates on the surface and in the lumen of the fibers. During the subsequent wet–dry cycles there is a “pump-like” effect with the consequent densification of the surface and lumen of the fibers, with products with high alkalinity (mainly calcium hydroxide) (Figure 12).

Other authors stated that the mineralization process is due to a chemical reaction of the cellulose polymer in isosaccharinic acid due to the high alkaline medium of the matrix. The fraction of this acid reacts with calcium ions, giving rise to a precipitated salt. This process catalyzes new transformations of the cellulose polymer in acid and the formation of more salts, leading to a weakening of the cellulose fibers [72-74].

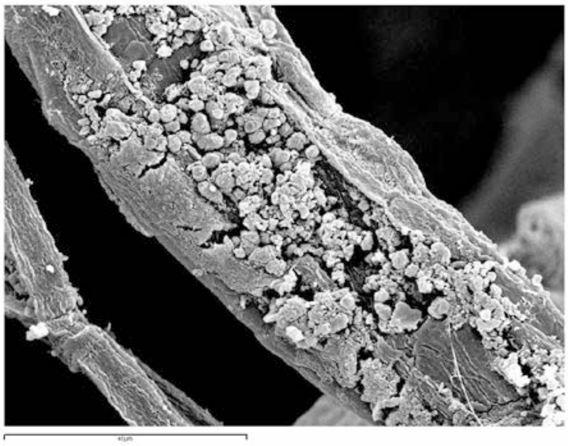


Figure 12. SEM micrograph showing cement hydration compounds in the lumen and surface of the fibers.

There are basically two strategies for improving the durability of the cellulose-fiber-reinforced cement-based composites. One possibility is to modify the composition of the matrix in order to reduce or remove the alkaline compounds. The second way to increase the durability of these composites is to modify the fibers with chemical or physical treatments to increase their stability in the cementitious matrix. Some of these treatments imply the use of chemical reagents and could be complex to apply in industrial processes. For this reason it is important to look for simple strategies which can be easily implemented.

6.1. Modifying the matrix

There are basically two treatments for removing or reducing the portlandite content in the matrix: adding pozzolanic compounds or the carbonation process.

The pozzolanic reaction is done during the hydration process between the calcium hydroxide and the amorphous silica, producing hydrated calcium silicate, a very stable salt. The reaction is the following:

$$3\ Ca^{++} + 2H_2SiO_4^{\ 2-} + 2OH^- + 2H_2O \rightarrow Ca_3[H_2Si_2O_7](OH)_2.3H_2O$$

In OPC, the amorphous silica content is not enough to transform all the portlandite present into C-S-H gel. This excess of portlandite is desirable for stainless-steel-reinforced concretes, where the durability depends mainly on the alkalinity of the medium. However, as mentioned before, this alkalinity is the main drawback for the cellulose composites, which require the portlandite to be reduced or removed from the medium. It is therefore necessary to add pozzolanic compounds to the cement paste in order to promote the transformation of portlandite into C-S-H gel. There are several pozzolanic additions, such as microsilica or silica fume, metakaolin, blast furnace slag or fly ash among others. Depending on the reactivity, it will modify the matrix in different manner.

Toledo Filho et al. [11] studied the partial replacement of OPC with undensified silica fume and blast-furnace slag (10 and 40% by weight of OPC) to reduce the alkalinity of the matrix as well as the content of calcium hydroxide. The results obtained indicated that the treatment of the matrix with undensified silica fume was an effective means of slowing down the strength loss and embrittlement of the cement composites. Nonetheless, the blast-furnace slag did not prevent the deterioration over time of the composites.

Mohr et al. [48] evaluated the performance of softwood kraft pulp fiber composites containing a variety of supplementary cementitious materials such as silica fume (SF), ground granulated blast furnace slag (SL), class F fly ash (FA), Class C fly ash (CA), metakaolin (MK) and proprietary blends of raw and calcined diatomaceous earth and volcanic ash (DEVA). They also studied different dosages in binary, ternary and quaternary blends prior to and after exposure to wet–dry cycling. They found that the composites containing 30% SF, 50% SF, 90% SL, and 30% MK apparently eliminated degradation due to wet–dry cycling. Ternary and quaternary blends of 10% SF/70% SL, 10% MK/70% SL, and 10% MK/10% SF/70% SL also prevented composite degradation due to a reduction in the calcium hydroxide content and the stabilization of the alkali content.

Toledo Filho et al. [43] analyzed the effect of the replacement of OPC with calcined clay in order to produce a matrix totally free of calcium hydroxide on the durability of sisal mortar laminates. They found that the long-term embrittlement of the composites was completely avoided through the use of this CH-free matrix (with 50% calcined clay as partial replacement of OPC). Therefore, the use of a CH-free matrix seems to be a promising alternative for increasing the durability of sisal fiber-cement-based composites with aging. In a recent study these authors [41] also found that OPC replacement with 50% of amorphous metakaolin led to a significant reduction of the calcium hydroxide formation.

Accelerated carbonation is the other alternative for increasing the durability of the cellulose cement composites which has been studied. Carbonation allows the quick reaction of $Ca(OH)_2$ with carbon dioxide (CO_2) resulting in $CaCO_3$. This process also has an influence on the mechanical properties of the composites, increasing strength and reducing the specific energy and water absorption. This process is usually done in humidity chambers with enriched CO_2 atmospheres. One interesting possibility which has been less studied is performing this accelerated carbonation under supercritical carbon dioxide (SC-CO2) processing conditions.

Toledo Filho et al. [11] studied the effect of accelerated carbonation on cement composites reinforced with sisal and coir pulp fibers. They found that carbonation of the specimens for 109 days was a promising alternative for increasing the durability of cellulose-cement-based composites. Tonoli et al. [24] also evaluated the effect of accelerated carbonation on the performance of sisal pulp reinforced cementitious composites after aging. They found that accelerated carbonation was an effective method to maintain the MOR of the specimens after 480 days in a laboratory environment. The same research group [28] analyzed this effect on cement composites reinforced with eucalyptus pulp. They concluded that accelerated carbonation could be considered as a viable curing condition when looking for durable eucalyptus cellulosic pulp reinforced cement-based composites. The properties of the composites were maintained after accelerated and natural aging, indicating their improved durability. The authors concluded that the decrease in the alkalinity of the cement matrix, lower porosity, and smaller average pore diameter associated with the densification of the matrix for the higher precipitation of $CaCO_3$ could explain the mitigation of the composite degradation.

Similarly, Soroushian et al. [52] analyzed the durability of CO_2-cured cement composites reinforced with softwood kraft pulp after 25 accelerated wet–dry cycles, after repeated freeze–thaw cycles, and after warm-water immersion. They concluded that carbonated boards showed reduced capillary porosity, increased $CaCO_3$ content and improved bonding. Furthermore, under diverse accelerated aging effects, carbonated boards also provided improved longevity and weathering resistance.

6.2. Modifying the fibers

The other strategy for improving the durability of cement composites consists in the physical or chemical modification of the fibers with the aim of optimizing the fiber-matrix adhesion and making them less sensitive to the matrix composition and environmental humidity.

A cheap and simple method successfully used by our research group to obtain more durable cement composites is the previously-mentioned hornification of cellulose fibers [15][34]. Hornification is an irreversible effect which occurs on fibers subjected to drying and rewetting cycles principally. Hornificated fibers have higher dimensional stability and lower water retention values. We found that the prior hornification of the fibers improved the durability of cement mortar composites, although it did not prevent the partial loss of their mechanical reinforcement. Around 13% (pinus pulp) and 21% (cotton linters) higher values of flexural strength and around 20% (pinus pulp) and 10% (cotton linters) higher values of compressive strength relative to the untreated fibers were obtained for the aged composites [34]. We also found that the lower permeability of the fibers of cotton linters resulted in lower degradation of the fibers and, as a consequence, less loss of resistance in the aged composites. The permeability of the pinus kraft pulp fibers, with pits on their surface, facilitated degradation in the interior of the fibers and, as a consequence, the loss of resistance was higher than that in the cotton linter fibers. This same treatment has been successfully used by Toledo Filho et al. in sisal reinforced cement composites [68][69][75]. The hornified sisal fiber composites presented a multiple cracking behavior under bending and direct tension loads as shown in Figure 13.

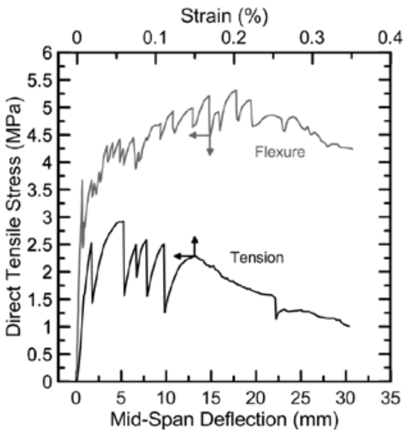


Figure 13. Load-deflection vs. tensile stress-strain response for hornified sisal fiber reinforced cement composites.

Tonoli et al. [24] evaluated the influence of the refinement intensity of sisal pulp on the mechanical performance of composites after wet–dry accelerated aging cycles. They found that pulp beating played an important role in composites subjected to accelerated aging tests. Toughness was greatly decreased with accelerated aging cycles, respectively to 29 and 12% of its original value for composites with unrefined pulp and medium refined pulp. In contrast, composites with the most refined pulp presented an increase in toughness after 100 aging cycles. The improved surface contact area after refining contributes to the enhanced adhesion of the sort fibers, despite the increase of the composite rigidity caused by a supposed mineralization or embrittlement of microfibrils after aging. The same authors also analyzed the influence of refinement, but with hardwood fibers [23]. In this case, they found that the mechanical performance of the composites after accelerated aging decreased with refining. However, toughness of composites with unrefined pulp was preserved after aging. They also found that after 200 accelerated aging cycles, the composites with unrefined eucalyptus pulp presented an improved mechanical performance in relation to the composites with pinus pulp. They observed that the short eucalyptus fibers were better distributed than pinus fibers and the bridging fibers shared the load, transferring it to the other parts of the composite. The consequence was the maintenance of MOR and toughness after 200 accelerated aging cycles in composites with unbleached eucalyptus pulp.

Mohr et al. [16][17][47] analyzed the effect of some treatments – beating, bleaching, initial drying stage and treatment of the pulp (kraft or thermo-mechanical) – of softwood kraft pulp fibers on minimizing composite degradation. They found that the beating and drying state of the fibers did not appear to significantly affect the mechanical behavior of the composite after wet–dry cycling exposure. Bleached fibers exhibited a more accelerated progression of fiber mineralization than unbleached fibers for low numbers of wet–dry cycles. Similarly, they also observed that in general, losses in mechanical properties progressed more slowly in composites made with thermo-mechanical pulps than in kraft composites.

On the other hand, Toledo Filho et al. [11] analyzed the effect of immersion of long sisal fibers in slurried silica fume prior to their incorporation in the matrix. They found that it was an effective method for improving the strength and toughness of the composites with time. The presence of silica fume in the fiber-matrix interface appeared to create a zone of low alkalinity around the fiber which delayed or prevented the degradation of the fiber by alkaline attack or mineralization through the migration of calcium products.

Finally, Tonoli et al. [29] evaluated the effect of surface modification of eucalyptus kraft pulp with silanes on the durability of the fiber-cement composites.

They found that after 200 aging cycles, composites with aminopropyltri-ethoxysilane APTS-treated fibers presented lower water absorption and apparent density compared with materials made with unmodified and methacryloxypropyltri-methoxysilane MPTS-grafted fibers. Despite this, they found that accelerated aging cycles decreased MOR and the toughness of the composites regardless of the treatment initially applied to the cellulose pulp. Non-mineralized filaments in composites with MPTS-modified fibers led to less damage in toughness and in final specific deflection after accelerated aging than in the other composites.

7. Concluding remarks

This review presents the research done in the last few years in the field of cement-based composites reinforced with cellulose fibers, focusing on their composition, preparation methods, mechanical properties, and strategies to improve fiber-matrix bonding and composite durability. The main conclusions are as follows:

1. Softwood and sisal pulps and sisal strands are the most commonly studied fiber form for preparing cellulose cement composites. Other pulps from eucalyptus, agricultural waste, cotton, or staple fibers like flax or hemp, among others, have also been studied to prepare cement composites but to a considerably lesser extent.
2. To adequately disperse the fibers in the matrix is necessary to obtain cement composites with good mechanical performance. This fact conditions the manufacturing methods which consist mainly of variations of the traditional Hatscheck method. Other newer methods are extrusion of pulp cement mixtures and laminates with long fibers or sheet-like structures. Extrusion allows the alignment of the pulp fibers in the machine direction and the lamination methods allow reinforcement with semi-finished products, such as unidirectional long fibers, to ensure a higher level of enforcement in the desired direction.
3. Since cellulose cement composites are manufactured in the form of small thickness panels, the most appropriate method of mechanical testing is the four-point bending configuration.
4. Different treatments can be used to improve the durability of cellulose cement composites: (a) by pozzolanic additions, either directly introduced into the mass of the cement or applied to the fibers, and/or through curing under a CO_2

atmosphere; (b) by refining the pulps with hornification treatments or chemical surface treatments, such as silanes.

Cellulose cement composites with good mechanical properties and high durability have been developed in the last decade. The main challenges for the near future are to further improve the durability and the mechanical performance of these composites without increasing the costs of production, while developing ecofriendly technologies.

Acknowledgements

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