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Treatments of plant biomass for cementitious building materials – A review

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Abstract

The use of plant biomass for developing energy efficient and low cost construction materials is an emerging field in building construction and civil engineering. Although the biomass-based cement and concrete composites have several advantages, such as low densities, low amount of CO₂ gas emission, good thermal and acoustic insulation, there are also disadvantages or open questions like the durability of biomass in alkaline cement matrix, the high absorption of water and the cement-biomass compatibility, all deteriorating concrete mechanical properties, which are already intrinsically low due to the low mechanical properties of biomass-based fillers. This review gives the necessary basis in plant structure and composition for understanding how and why many treatments tested on biomass for overcoming the above-mentioned difficulties are acting. This paper reviews research papers and patents on the treatments tested to improve the mechanical properties, durability and compatibility of biomass for its use as concrete fillers for building materials.

Keywords: concrete, cement, biomass, treatment, durability, mechanical properties.

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1. Introduction

Cement concrete is the most widely used engineering material because of three primary reasons: (1) excellent resistance to water, (2) the ease to form structural concrete elements into a large variety of shapes and sizes, and (3) usually being the most readily available material [1]. Low maintenance, good fire resistance and cyclic loading resistance are some of other considerations that favour the use of conventional concrete structures. However, the fact that concrete is brittle, its cracking and shrinkage tendencies (both drying and thermal shrinkages), and its low tensile strength are serious disadvantages in structures built with concrete. When strength of concrete is increased, its brittleness is also increased [2] and cracking is induced, which could lead to serious damages to the concrete [3]. To overcome this problem, the combination of regular concrete with reinforced steel bars is a common strategy designed so that the two materials act together to resist tensile forces. Unluckily,

the high permeability of reinforced concrete, that allows water and other aggressive elements such as chloride to penetrate, or slow carbonation, is responsible for the corrosion of steel bars [4–6]. It leads to the infrastructure deterioration and to severe industrial and natural environment drawbacks.

Concrete consists of a binding medium, which is usually cement, water, aggregates, and reinforced steel bars. The productions of these construction materials are expensive and consume an enormous amount of thermal and electrical energy as well as non-renewable resources. Thus, it is not possible to use them in very low cost housing, especially in developing and under-developed countries.

Another crucial aspect when using concrete-based structures is their thermal properties. At least in Europe, there is a strong move towards having better thermally insulated housings to reduce energy consumption while keeping good comfort conditions in buildings, with EC and EU National directives and regulations forcing builders to improve their construction methods. The design of energy-efficient buildings requires to mastering the control and the understanding of the thermal performances of structures. This is a complicated problem for concrete with different facets like the need to have the lowest thermal conductivity to reduce heat loss and a very high thermal inertia to store heat. All published work concludes that what controls mostly the thermal conductivity of concrete are the type of aggregate (having itself its own thermal conductivity characteristics), the porosity and the moisture content [7]. Classical concrete blocks prepared with mineral aggregates have thermal conductivities λ in the range of 1.5 to 3 W/m.K, decreasing down to about 1 W/m.K when adding various mineral admixtures [8]. Such values impose to add either very efficient or thick insulating materials to concrete structures.

In the early 1970's, the elimination of a wide range of products based on fibre silicates (asbestos) was initiated due to the cancer health risks [9,10]. Fibre-cement composite was a major user of asbestos but now this reinforcing mineral fibre can be replaced by synthetic fibres such as polypropylene using the air-cured Hatscheck process [11]. However, the production of such polypropylene fibres requires amines (ultraviolet stabilizers) and phenol compounds (anti-oxidant), and high energy consumption [12]. In addition, when concrete is deposited or dumped, polymer fibres are not decomposing, these polymers being not biodegradable [12,13].

With regard to the environmental aspect and economic viability, it is clear that the replacement of reinforced steel bars, mineral aggregates and asbestos or inorganic fillers by biomass-based materials could be an important step to alleviate some of the drawbacks and problems cited above [9,14,15]. Hence, researcher groups have been focusing their investigations on enhancing the engineering properties of cementitious products containing biomass, including preparation procedures, biomass

treatments, long term durability, ease of production, mechanical and thermal properties as well as environmental impacts. Numerous articles have been published on the physical, mechanical, structural and functional properties of these biomass-based building materials made of concrete. The use of biomass to replace conventional materials seems to be a feasible solution to solve the problem of pollution, to reduce the amount of CO₂ emission and to develop more energy efficient and cost effective durable construction materials.

2. Composition, properties and availability of biomass

Biomass is the matter based on carbon, hydrogen and oxygen produced by Nature. Chemical compositions and structure of biomass are very variable and are influenced by origin, climatic conditions, age and location in the plant [16–19]. The components of biomass are forming a chemical complex of cellulose, lignin, hemicelluloses, inorganic substances and extractives such as pectins, fats, waxes and other water-soluble substances. Among all these components, cellulose, hemicelluloses and lignin are the three principle main constituents with regard to the physical properties of the biomass. These polymers are not uniformly distributed within plants and their concentrations change with plant species and for a given species with many factors, such as type of tissue, climate, soil or date of harvesting. Before describing in more details the structure of plants and its various parts used for preparing concrete materials, it is necessary to precise the meaning of the term “fibre” used in many studies, but describing many different objects depending on the context.

What is added in cement, water, sand and admixtures to prepare a plant-based concrete is a part of a plant or a tree, never the whole plant. All ligno-cellulosic plants and trees are composed by a complex structure as shown in Figure 2 in reference [20].

A plant may have stems, leaves and fruits. Each of these parts has a specific biochemical composition and structure which are related to their function in the plant. Composition and structure depends thus on the part of plant which is considered. The structural strength of plant is given by the “strong” polymer, cellulose. Plants are composed by millions of cells, each one separated from its neighbours by a cell wall. For example, a wood piece is composed of an assembly of cells glued together with lignin. Each cell is surrounded by walls, themselves composed of cellulose, hemicellulose and other compounds. Cells are differentiated to insure different functions. Cellulose is biosynthesized in the plasma membrane of each cell in the form of a small, long filament

comprising a small number of cellulose chains, in the order of 24-36 chains per filament [21]. This filament could be called a fibre. These filaments agglomerating in larger filaments to form the cell wall are usually called nanofibres. These cellulose nanofibres (or NFC) can be extracted from plants and trees and they form a very active research area, due their intrinsic high mechanical performances or other properties [22,23]. These cellulose nanofibres will be wrapped in a very complex manner around the cell membrane to build the thick secondary cell wall, together with lignin and hemicellulose. This wall is commonly described as formed by cellulose microfibrils interconnected by amorphous lignin and hemicellulose [19]. This forms another type of fibre, like for example the ones extracted from wood which are used for paper making, shown on Figure 1. Similar types of such complex structural cell walls with or without hemicellulose or lignin traces can be found in all fibres including cotton fibres. Such fibre-shaped cell wall structures can be extracted as groups of fibres, with various amounts of lignin and hemicellulose, from all plants (like flax and hemp).

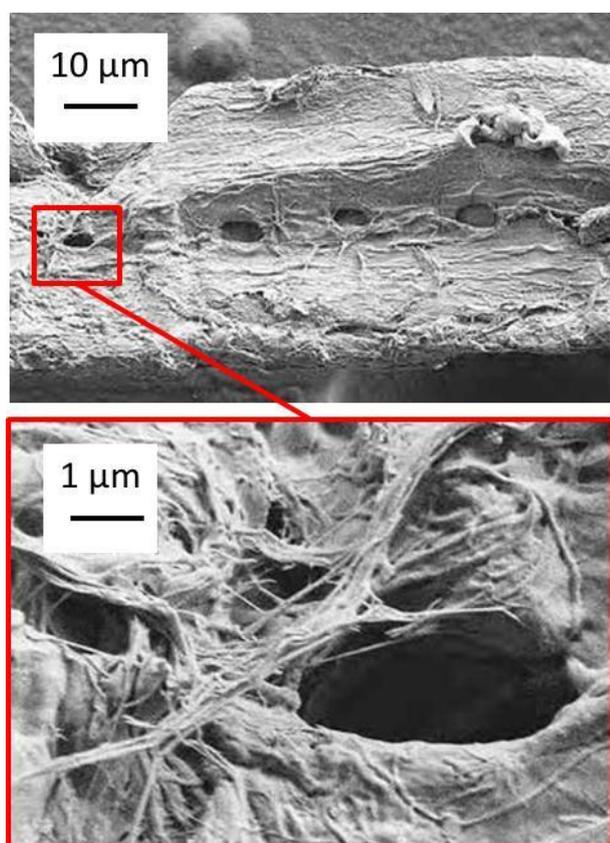


Figure 1. Spruce bleached sulphite pulp fibre observed by scanning electron microscopy. Top: this fibre is the wall of a single cell, where the nucleus was in the central part. What we see here is the outside part of this fibre. Bottom: the picture is showing the array of microfibrils of less than 100 nm thickness attached to the surface, surrounding a pit opening (Reprinted with permission from the PhD dissertation of Nuno dos Santos [24]).

The location of the plant from where these “fibres” are extracted can greatly vary. Fibre-like plant pieces can come from organs having no structural role like cotton, from cell structures or various natures as in wood, from the inner bark situated after the outside bark skin of plants (bast fibres, extracted from plants like flax, hemp, or ramie). They are usually soft and flexible. Fibre-like pieces can be extracted from other parts, like leaves. This is the case for curauá or banana. Fruits can also provide fibre-like pieces like in coir, where fibres are extracted from the husk, between the internal shell and the outer coat of a coconut. Another option is not to extract anything from the plant but to break its stem into fragments. These fragments can be of various shapes, with a low aspect ratio like in wood or with a larger axial ratio like in miscanthus. In the latter case, they are called often miscanthus fibres in scientific publications.

The method of extraction is also very variable, influencing strongly the chemical composition of the fibre-like pieces. It can vary from mechanical extraction (like in leaf fibres) to the use of chemical treatments like in wood cell fibres used for paper making or through natural or artificial enzymatic extraction like in most bast fibres.

As can be seen, the word “fibre” and in particular “cellulose fibres” can encompass very different plant parts, having very different physical and mechanical properties. When used associated with a plant name, like bamboo fibres, it is very unclear if these fibres are elongated pieces of broken stems or cellulose fibres extracted from bamboo, and in this latter case, which exact type of extracted fibres it is. In this review, we will be careful to avoid using the term fibres without precisising what it means.

Table 1 gives the compositions of three main components of several lignocellulosic plant parts. It shows that composition can vary over a very large extent. Composition is in addition not the only important parameter. The structure of the fibre-like piece is also very variable and is influencing the mechanical properties of the pieces. Surface properties are also important since most plants are covered with a thin layer of chemical compounds (like wax for example) in order to control the interaction of the plant with atmosphere.

Cellulose is the substance of biomass controlling the strength of the plant structure. Cellulose is a polymer made of D-anhydroglucopyranose units linked together by β -(1→4)-glycosidic bonds [25]. Each of the anhydroglucose units contains three hydroxyl groups at C-2, C-3 and C-6 positions, which are able to form hydrogen bonds with oxygen atoms. The hydroxyl groups and glycosidic bonds undergo the typical reactions for primary and secondary alcohols and are involved in degradation reactions. Cell wall cellulose fibres can swell to some degrees in water or aqueous alkaline media, which could be a problem when used in concrete. Cellulose is degraded or oxidized

in aqueous or non-aqueous acid media or in the presence of fungi or bacteria by cleavage of the glycosidic bonds. At temperature starting above 180 – 200°C, mainly between 250 and 300°C, cellulose suffers a thermal degradation leading to gaseous products and char.

Table 1. Proportion of cellulose, hemicellulose and lignin in various plant parts adapted from [17] and [26].

	Cellulose (%)	Hemicelluloses (%)	Lignin (%)
Coir (mechanically extracted from coconut fruit)	36 – 43	0.15 – 0.25	41 - 45
Cotton (hair with no structural function, collected as it is from the plant flower)	82.7 – 92	2 – 5.7	very low
Flax (bast fibre)	60 – 81	14 – 18.6	2 – 3
Hemp (bast fibre)	70 – 78	17.9 – 22	3.7 – 5
Jute (bast fibre)	51 – 72	12 – 20.4	5 – 13
Sisal (bast fibre)	43 – 88	10 – 13	4 – 12
Wood (broken from tree, mean values)	45 – 50	15 – 30	20 – 35
Values depends if it is hard or soft wood and on the location (tension vs compression wood for example)			
Wood cell fibres (dissolving pulp)	94-99	2-5	Very low

Hemicelluloses are low degree of polymerization branched hetero-polysaccharides present between the cellulose microfibrils in cell walls [17,19,27]. Hemicelluloses serve as an interface between cellulose and lignin and it is difficult to isolate hemicelluloses without modifying them. Their basic units are various hexoses (D-glucose, D-mannose and D-galactose), pentoses (D-xylose and L-arabinose) and small amounts of deohexoses (L-rhamnose and L-fucose) and uronic acids (4-O-methyl-D-glucuronic acid, D-galacturonic acid and D-glucuronic acid) [27]. In addition, an important part of hemicelluloses are acetyl groups. The types and compositions of hemicelluloses present in the cell wall vary significantly, depending upon plants, growth stages and conditions, and type of tissues. Hemicelluloses have a low thermal stability and they can easily be hydrolysed by

diluted acid, and highly soluble in alkali and susceptible to fungal attack. Hemicelluloses are the weakest point when dealing with concrete preparation.

Lignin is a hydrophobic high molecular weight condensed aromatic substance and its composition and structure vary from one type of plant to another [16]. The structure, and thus the reactivity of lignin are different not only between kinds of plants, but also between plant tissues, types of cells and cell wall layers. The molecular chains are built up from three main units, namely guaiacyl, syringyl, and *p*-hydroxyphenyl moieties [28–30]. Lignin has an enormous number of ether (C-O-C) and carbon-carbon (C-C) linkages. It forms a three-dimensional network, forming one of the most complex structures among naturally occurring polymers. Depending upon its units, three main types of lignin are differentiated: guaiacyl lignin (or softwood lignin), syringyl - guaiacyl lignin (or hardwood lignin) and HGS-lignin (Hydroxy phenol, Guaiacyl, Syringyl or grass lignin) [29]. Lignin makes the cell wall hydrophobic, and the presence of lignin can help to protect lignocellulosic materials from microbial degradation. Due to its sophisticated structure having a mixture of aromatic and phenolic moieties, lignin can be involved in many reactions such as hydrogenolysis, hydrolysis, condensation and oxidation etc. [28]. Lignin can be removed from lignocellulosic materials by chlorination to form a soluble chloro-lignin [16] or by reaction with hot alkali in pulping processes [31].

Biomass has a high degree of porosity. With the presence of the numerous hydroxyl groups of cellulose and hemicelluloses, biomass is also highly hygroscopic, the attraction of water molecules leading to an increase in dimension upon immersion [17,18]. The presence of hydrophobic lignin can, on the other hand, decrease moisture absorption and hinder the penetration of water into the cell wall.

In terms of thermal and electrical properties, biomass is a good resistance material. These characteristics (as well as its mechanical properties) are affected by the moisture content and hence, the relative humidity of the surrounding atmosphere. Table 2 lists data of physical and mechanical parameters of some natural and other fibres-like pieces or synthetic fibres [17]. In general, biomass fibre-like pieces exhibit similar density and a small extension at break. By the opposite, biomass presents large variations in tensile properties.

The primary advantages of using biomass in building materials are low density, good thermal insulation and low cost. The utilization of biomass can lead to energy saving, conservation of non-renewable resources and protection of the environment.

Table 2. Physical and mechanical properties of various fibres and plant-based fibre-like pieces [17]

	Density (g/cc)	Extension at break (%)	Tensile strength (MPa)	Young's modulus (GPa)
Aramide	1.4 – 1.45	3.3 – 3.7	3000 – 3150	63.0 – 67.0
Carbon	1.40 – 1.75	1.4 – 1.8	4000	230.0 – 240.0
E-class	2.50 – 2.55	2.5	2000 - 3500	73.0
Cotton	1.50 – 1.60	2.0 – 10.0	287 – 597	5.5 – 12.6
Flax	1.40 – 1.50	2.7 – 3.2	343 – 1035	27 – 80
Hemp	1.40 – 1.50	1.3 – 4.7	580 – 1110	3 – 90
Jute	1.30 – 1.50	1.4 – 3.1	187 – 773	3 – 55
Sisal	1.30 – 1.50	2.0 – 2.9	507 – 855	9.0 – 28.0

Biomass is relatively cheap, renewable, and plentifully supplied all over the world. It can come from either woody crops, vegetable plants or generated from agricultural industry by-products. Harvesting and processing generates huge quantities of agricultural by-products such as sugarcane bagasse, rice husk, straw, cotton stalk, oil palm shell or coconut husk [14,15]. The disposal of these agro-waste solids is becoming a major problem, not only causing pollution but also land filling. If they are not burned to recover energy, a possible solution is to use these lignocellulosic side-products as construction materials.

3. A look at the biomass used for cement and concrete composites

There are currently a large number of studies undertaken to use biomass either from dedicated crops or from agro-waste as substitutes for aggregates and reinforcements in cement and concrete composites. They may have the potential to lead to new and economically viable construction materials [9,10,14,15,32–34].

3.1. Types, sizes and amount of biomass used in cementitious products

Numerous biomass materials have been investigated for their uses in building materials in order to identify their prospective value as added products. The majority of biomass reported in published papers or patents was industrial by-products collected from various sources. They were grinded or cut into suitable sizes to be used in construction materials.

Table 3 lists a selection of biomass sources used as substitutes for reinforcement or aggregates in cement and concrete materials, together with their sizes and amount. Much more biomass materials were tested such as bamboo [35–40], sisal fibres [32,41], jute fibres [42], pineapple leaf fibres [32], sugarcane waste fibres [43], cork granular [44], curauá [45,46], cattail (typha) [47] and cellulose pulp [48–52] etc. They provide alternative solutions to the problem of limited supply of non-renewable mineral resources for construction. The effects of aggregate size and strength, proportions, component ratios as well as curing and operating conditions have been intensively studied.

Table 3. Types, sizes and amounts of biomass used in cement and concrete composites

References	Kind of biomass	Size (mm)	Water/binder ratio	Amount of biomass
[53]	Oil palm (coconut) shell	5 – 15(20)	0.5 and 0.75	0 – 25 – 50 – 75 – 100% of coarse aggregate (stone)
[54]	Oil palm shell (OPS)	max. 12.5	0.41	Sand/OPS ratio 2.22 by weight
[55]	Oil palm shell	1.5 – 2.5	0.41	0.77 (weight proportion)
[56]	Palm fibres (21.13µm)	30 (length)	0.43	0.25 – 0.5 – 0.75 – 1.0 vol%
[57]	Palm fibres (leaves)	30 (length)	0.34	0.05 to 0.15 wt% (of total wet solid)
[58]	Date surface palm fibres (around the trunk)	15 and 60	adjusted to the mix with fibres percentage	percentage of fibres was varied but the mass of fibres plus aggregates was maintained constant
[59]	Hemp shives	4 – 8 – 9	49 – 51% (water content)	16 – 17 wt%
[60]	Hemp fibres, wheat straw, Miscanthus	40	0.67	0.19% by weight (4.5 kg/m ³)
[61]	Hemp fibres	30 (length) 0.6 (diameter)	0.68	0 – 0.5 – 0.75 – 1 vol%
[62]	Coconut shell	max. 12.5	0.42 to 0.72	Shell/cement ratio = 0.55 – 0.6 – 0.65
[63]	Coconut fibres	25 – 50 – 75	0.48	1 – 2 – 3 – 5% by cements mass
[64]	Coconut fibres	20 – 30 (length) 0.32 (diameter)	0.42	0.6 – 1.2 – 1.8 – 2.4% based on binder volume
[65]	Coconut shell	max. 12.5	0.42	332 kg/m ³
[66–68]	Flax shives	4 – 8 (length) 0.6 – 1.3 (width)	0.5 or 0.75	shive to cement volume = 4

Table 3. (cont.)

References	Kind of biomass	Size (mm)	Water/binder ratio	Amount of biomass
[69]	Flax stem fibres	20 – 30	0.58	0.5 and 1 % (v/v)
[70]	Flax straw fibres	10 – 19 – 38		0.05 – 0.1 – 0.3% by volume
[49]	Eucalyptus kraft pulp	0.81 (length)		5 wt% (or 9 vol%)
[50]	Sulphite pulp fibres	1.2 – 1.5	1	5 – 10 – 15% by binder mass
[51]	Micro-cellulose fibres (recycling of cardboard)	1.1 (length) 0.045 (diameter)	0.35	14 – 21 – 28 – 41 – 83 – 138% volume fractions of fibre to cement
[71–73]	Wood shaves	0.1 to 8	0.59	0 – 160 kg/m ³
[74]	Kenaf bast fibres	25 – 38	0.35	1.2 – 2.4% (volume content)
[75]	Lechuguilla fibres	25 and 50	1	0.25 – 0.50 – 0.75 – 1.0 (volume fraction)
[76]	Lechuguilla fibres	20 – 30	0.35 and 0.65	1 vol%

In most of the studies reported in literature, biomass materials were used as collected. The preparation, curing conditions and casting of concrete mixtures containing biomass are in most cases similar to the normal concrete mix design and carried out according to different standard specifications. However, in some cases, washing or chemical pre-treatment stages were applied to remove undesired substances present in the biomass materials, improve various properties and ease processing.

3.2. Properties evaluated

The mechanical strength, bond behaviour and elasticity modulus of hardened cements and concretes are the most important assets that are normally evaluated, along with some durability properties and other characteristics such as thermal conductivity and water absorption (Table 4 and Table 5). The assessments were done in accordance with the standard procedures used for conventional concrete and cementitious products.

The investigations have proven that concrete made with biomass aggregates exhibit the following positive properties:

- Reduction in density of hardened concretes [77];

- Sufficient strength to be accepted as structural lightweight concrete if suitable contents of biomass has been used [78,79] (as illustrated in Table 4);
- Enhancement in flexural strength and ductility [41,61,80] and fracture energy [60];
- Good indoor quality and energy savings, especially in winter [81];
- Good thermal insulation [43] and acoustical absorbency [59].

Table 4. Mechanical properties of cement and concrete composites containing biomass reported in the literature

References	Kind of biomass	Compressive strength (MPa)	Flexural strength (MPa)	Splitting strength (MPa)	Modulus elasticity (GPa)
[43]	Coconut coir fibres	27.8		3.28	
	Sugarcane bagasse	27.6		3.92	
[51]	Micro-cellulose fibres	30 - 60	6 - 12		
[53]	Palm kernel shells	15.0 - 25.0			
	Coconut shells	15.0 - 27.5			
[54]	Oil palm shells	20.1 – 24.2			
[57]	Palm fibres (leaves)	60.2 – 65.0	9.4 – 9.9	3.8 – 4.4	
[60]	Hemp fibres	34.6			
	Wheat straw	31.7			
	Miscanthus	30.5			
[61]	Hemp fibres	18.9		2.2	22
[62]	Coconut shells	29.95 - 26.70	4.26 - 4.68	2.38 - 2.70	
[63]	Coconut shells	30 - 45			29.31 - 37.85
[64]	Coconut fibres	72.96 - 74.00			
[77]	Oil palm shells	36.70 – 37.41		1.95 – 2.10	10.05 – 11.15
[78]	Oil palm shells	20.12 – 24.22	2.75 – 4.00	1.78 – 2.41	7.0 – 7.6
[82]	Oil palm shells	42.8 – 48.3			
[83]	Oil palm shells	26.98 – 37.79		1.98 – 2.35	7.08 – 10.90
[84]	Coconut shells	25.0 – 27.5			
[85]	Hemp shives	0.15 – 0.83		0.0216 – 0.113	0.013 – 0.049
[86]	Hemp fibres	13.88 - 35.22	3.10 -5.18		
[87]	Hemp shives	0.18 - 0.80	0.832 - 1.209		0.004 - 0.035
[79]	Rice husk	17.6 - 37.5			

Table 5. Durability-related and other properties of cement and concrete composites containing biomass reported in the literature

References	Shrinkage	Water absorption	Thermal properties	Weathering	Freeze-thaw resistance	Ultrasonic pulse velocity	Corrosion behaviour	Permeability	Initial surface absorption	Sound
[84]						√				
[73]	√		√							
[88]							√			
[56]								√ (oxygen)		
[78]	√								√	
[41,86,89]		√								
[85]		√			√					
[64]								√ (chloride)		
[52,61,72,87,90–92]			√							
[48,50,53,82,93]		√								
[58]		√								√
[59]										√
[79]		√	√		√					
[66–68,73]	√		√							
[49]	√	√								
[71]	√									
[43]					√			√ (sulphate)		
[94]				√						

Numerous works have been performed to value the use of biomass in cementitious materials, considering that there is a vital need to translate present knowledge into downstream commercial activities. However, the development and practical applications of these materials are still under a critical evaluation due to several problems that have to be tackled, as it will be discussed in section 4.

3.3. Some practical uses of biomass-based cement and concrete composites

Although biomass-based cementitious composites are still under investigation, some efforts have already been conducted in order to use these materials in practice and to prove that it is possible to apply them in constructions and buildings.

Among the biomasses used for investigation, hemp, and more precisely shives, has been proven to be a good candidate. A mixture of hemp, sand and an hydraulic binder and the resulting materials, manufacture under different trade names, leads to a light weight building materials with a low compressive strength (around 1 MPa) but good thermal insulation properties [95–98]. This imposes to use it together with a structural frame which will support the vertical load of the building. Hemp-

based concrete can be used to make various surfaces in constructions: roofing insulation, walls and floors [99,100]. Depending on each type of applications, its properties can be tailored to meet desirable criteria [101,102]. Called Hempcrete, mixtures of hemp shives mixed with a lime-based binder have been used to build houses [103], as shown on Figure 2.



Figure 2. A hemp-based house built in Florida (with permission from Bob Clayton, Florida, USA) [103].

A research group at the Polytechnic University of Hochiminh City (Vietnam) built a house (Figure 3) with coconut shell reinforced concrete using conventional building processes applied for ordinary houses [104]. They believed that the house can be used as a mobile home, as temporary shelters or to build houses in flooded areas.



Figure 3. Coconut reinforced concretes: a) a concrete block, b) the concrete panels and c) the house built from them (with permission of Nguyen Tan Khoa and his supervisor (Dr. Le Anh Tuan) [104].

Using mountain pine wood from trees killed by the mountain pine beetle, Sorin Pasca and Dr. Ian Hartley from the University of Northern British Columbia [105] developed a wood-based concrete building material with many desirable physical properties to be used for decorative purposes, from countertops, tables, benches to flooring (Figure 4).



Figure 4. Various applications of mountain pine wood concretes [105]. With permission from Pasca, S & Hartley, ID 2012, 'Beetlecrete – An attractive solution to mountain pine beetle epidemic', Proceedings of International Inorganic-Bonded Fiber Composites Conference (IIBCC 2012), 10-14 September, 2012, Acton, Australia. (Available from: www.proceedings.com, Item #20276)

Miscanthus x giganteous, which is well-known to be used as biomass energy crop, has also been utilized to produce various construction materials, from isolation panels to bio-concrete blocks [106–109]. Thanks to its ability to fix CO₂, one hectare of miscanthus used for building can store 40 tonnes of CO₂, helping to reduce the greenhouse gas emission. With good capacity of thermal and acoustic insulation, these materials can be used for noise barriers or low energy consumption houses (Figure 5). Depending on the binders used, the compositions of fresh concrete and the nature of miscanthus, the concrete can archived the compressive strength at 7 days ranging from 0.95 to 5.84 MPa with thermal conductivity of 0.7 W/m.K at 20%RH and 20 to 60°C [authors' work].



Figure 5. a) Miscanthus-based mix and block (author's work) and b) a miscanthus based noise barrier and (c) a house built with miscanthus concrete [106]. With authorisation of asbl ValBiom, Croix du Sud 2, bte 11, 1348 Louvain-la-Neuve, Belgium.

In general, it is believed that biomass-based cement and concrete composites can be used naturally, pleasantly and efficiently as materials for building houses, decorations and/or heat/acoustic insulations [110,111].

4. Difficulties arising when using biomass in cement and concrete composites

As mentioned in previous sections, a wide range of natural plant pieces and agro-wastes were studied for construction and building material applications. They show great potential as inexpensive and renewable materials able to contribute to save conventional resources. However, although short-term properties of biomass-cementitious materials are promising, their long term engineering performance needs to be ensured since the service life required is long, generating several challenges to both science and technology to use biomass in cement matrices [112]. There are only a small number of published studies assessing long-term durability of biomass-based concrete [43,84,113].

The main drawback to the use of biomass in a building material is the durability of plant parts in the cementitious matrix due to its alkaline character ($\text{Ca}(\text{OH})_2$). The most common binder used in construction is Portland cement which is essentially a mixture of tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$, C_3S), dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$, C_2S) and tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$ abbreviated C_3A) [114,115]. When cement reacts with water, the hydration of cement occurs and yields hydrated products including calcium-silicate-hydrates (C-S-H) and calcium hydroxide ($\text{Ca}(\text{OH})_2$ or CH). The major components of biomass are cellulose, hemicellulose, lignin and other extractives, which properties having been given in Section 2. Alkalis readily react with extractives and hemicellulose, but have little effects on lignin at low concentration and ambient temperature. However, lignin is soluble in hot alkali, oxidisable and it easily condensates giving a number of coloured products. During mixing to prepare cement mortar or concrete, the chemical reaction between cement and water releases heat [114,115]. Due to the increased temperature and the alkalinity of hydrated cement, the dissolution of low molar mass carbohydrates from biomass is promoted, weakening the plant piece structures [9,33]. In addition, hydrated cement products can degrade cellulose in some extent, leading to a further increase in the amount of soluble carbohydrates with aging. A research stated that after exposing coir, sisal, jute and hibiscus fibres in alternative wetting and drying cycles of continuous immersion for 60 days in water, saturated lime or sodium hydroxide, the four fibres suffered a substantial alteration of their chemical compositions [116]. The loss of substances like hemicellulose or lignin in plant pieces leads to their severe degradation which can in turn lead to a reduction in mechanical properties of concrete.

Another cause of degradation for lignocellulosic materials in hydrated cement medium is the mineralization of fibres by Ca^{2+} or other cations from the cement suspension [33,117]. This mineralization, due to the migration of hydration products, especially $\text{Ca}(\text{OH})_2$, to fibre lumen (lumen is the empty parts in the centre of the cell where the cell nucleus was sitting: after cell death,

it dries and leave an empty space), walls and voids, is associated with the embrittlement of the concrete [32].

Another aspect to consider is that sugar components, hemicellulose and lignin can contribute to the inhibition of cement hydration or delay the cement setting time [33,118–122]; even Eucalyptus pulp fibres which contain up to 85 wt% cellulose can reduce cement hydration rate [123]. Acid compounds released from biomass can also reduce the setting time of cement matrix [9]. Cement hydration, setting and hardening depend on the concentration of extracted chemical from biomass [119], their molecular weight and their stability in alkaline aqueous phase of hydrating cement [120].

In the case of sugars, overwhelmingly, it is concluded that sugars retard the hydration of Portland cement. A concentration as low as 0.03 – 0.15 wt% of sugar in cement paste can already delay the setting time [124]. The phenomenon was explained by the migration of sugar in the cement matrix, the capacity to absorb on Ca^{2+} products, preventing C_3S from hydration and transformation into C-S-H [118,122]. Consequently, the mechanical strength of the cement matrix was significantly changed. When higher content of sugar (≥ 0.15 wt%) was present, however, the cement setting time was dropped and if it was higher than 0.3 wt%, the setting was accelerated [125]. In addition, the effectiveness depends on the nature of sugars [122]. Non-reducing five-membered ring sugars, such as sucrose and raffinose, are the most effective retarder; while the other non-reducing sugars like trehalose and α -methyl glucoside are considered as non-retarders. The reducing sugars – glucose, maltose, lactose and cellobiose – are good retarders. The main saccharides of different biomass species are glucose, arabinose, xylose, galactose, rhamnose and fucose. The set-retardation actions of these saccharides, apart from glucose, have not been investigated systematically. A recent research showed that the retarding effect of glucose highly dependent on the chemical compositions of cement binder [126]. Binder with high amount of C_3A and C_3S is favourable since glucose will react with C_3A first, increasing the heat release and less available to retard the other components like C_3S and hence, reducing the retarding effect. If the binder contains C_4AF , the degree of retardation is also low. Thus, if the right cement compositions are used, the retardation effect can be overcome.

Being dimensionally instable when exposed to moisture, biomass-based materials are also posing a technical challenge for users of biomass in cementitious products. Water absorption, which was reported to be higher for biomass-based concrete than that of conventional concrete because of the presence of micropores in fibres, is another reason why the durability of biomass-based concrete decreases [9,14]. Water absorption leads to continuous volume change of the porous fibres inside cement matrix, causing interfacial damages and inducing concrete crack. The increase of

permeability of concrete is due to cracking at biomass interface leading to destructive effects on concrete.

Moreover, Bederina et. al. [71] found that with the addition of biomass pieces, shrinkage was higher due to the loss of free water and voids remaining inside concrete. The high variation of properties of natural materials is an additional disadvantage which could lead to unpredictable properties of concrete [9,86,112]. When chopped biomass pieces are used as fillers, their distribution in an homogeneous manner in cement matrix is a major issue [42]. Light natural materials may tend to segregate and float on the matrix surface.

All these problems have limited so far the applicability of biomass-based concrete although there were numerous research attempts and trial tests.

5. Overcoming the problems

The ability of lignocellulosic biomass fillers to resist external factors (e.g. variations of temperature and humidity, sulphate and chloride attack) and internal damages (e.g. alkalinity of binder, compatibility between fibres and cement matrix, volumetric changes) is controlling the durability of biomass based-concrete. Two main approaches have been followed to improve the durability of biomass: either the biomass filler is modified or the matrix is tailored for minimizing biomass disadvantages. The first approach is based on the protection of biomass fillers by coating or pre-treating them to avoid the destructive effects of alkali and water. Chemical treatments were also performed up to some desirable levels, needed for reaching good chemical bonding between fibre and matrix and high durability. The second approach is mainly the reduction of free alkalis in cement matrices obtained by developing low alkaline binders based on industrial and agricultural by-products. The following section will mainly address to the first approach, with a brief summary for the second one and other methods. As illustrated in Table 6 and Table 7 (bond strength, compressive and flexural strengths), some treatments enhanced the properties, while others reduced them significantly.

5.1. Materials modifications

The various treatments which were proposed are intended to limit water coming from external environment to reach the biomass filler in order to prevent the release of low molar mass carbohydrates in matrix. Several treatments were reported with some degrees of success.

Table 6. Behaviour of biomass in reinforced concrete from pull-out test

References	Kind of biomass	Treatment	Bond strength	Unit
[36]	Bamboo segments with no node	No treatment	0.52	MPa
		Negrolin + fine sand	0.73	MPa
		Negrolin + fine sand + wiring	0.97	MPa
		Sikadur 32-gel (adhesive)	2.75	MPa
[39]	Bamboo segments with node	No treatment	1.2	MPa
		Negrolin + fine sand	1.55	MPa
		Negrolin + fine sand + wiring	1.8	MPa
[127]	Red pine sticks	No treatment	0.186 ± 0.069	MPa
		Soaking in water 6h	0.303 ± 0.103	MPa
		Chromated copper arsenate treated	0.386 ± 0.138	MPa
		Chromated copper arsenate treated + 6h water	0.834 ± 0.165	MPa
	Lodgepole pine sticks	Soaking in water 24h	0.172 ± 0.048	MPa
		Chromated copper arsenate treated + 24h water	0.476 ± 0.048	MPa
	Jack pine sticks	No treatment	0.090 ± 0.021	MPa
Soaking in water 24h		0.250 ± 0.031	MPa	
Chromonium trioxide treated		0.356 ± 0.44	MPa	
[38]	Bamboo segments with knobs	No treatment	715 - 2868	lbs
		Sulphur +sand (one coat)	2315 - 3100	lbs
[128]	Bamboo rod	No treatment	pull out	
		Sulphur coated	2315	lbs
		Sulphur coated + wrapped with wire	2380	lbs

5.1.1 Coating or impregnation

The use of water-repellents on biomass-based fillers can reduce their water and free alkali absorption. Bamboo rod pieces have been impregnated in molten sulphur [38,128] or coated with a thin layer of epoxy [36,39] or adhesive [129] and then a coating of fine sand was applied. This method was considered effective in waterproofing and minimizing swelling-shrinking properties of bamboo rods as well as improving adhesion between bamboo rod surface and concrete by more than 100% (Table 6).

Table 7. Compressive and flexural strengths at 28 days of cementitious composites containing various biomasses with and without treatments

Reference	Kind of biomass	Treatment	Compressive strength at 28 days (MPa)	Flexural strength at 28 days (MPa)
[42]	Jute fibres	No treatment	51.7 ± 1.5	5.2 ± 0.3
		Alkali treatment prior to carboxylated styrene-butadiene copolymer emulsion coating	54.3 ± 1.6	5.7 ± 0.2
		Tannin and carboxylated styrene-butadiene copolymer emulsion coating	60.6 ± 1.2	6.4 ± 0.3
[50]	Waste sulphite pulp fibres	No treatment	7.22 - 8.98	2.78 - 3.61
		With the presence of nano-SiO ₂	9.42 - 13.82	3.62 - 4.58
[66]	Flax shives	No treatment	0.34 - 0.46	0.16 - 0.18
		Poly(polyethylene glycol-co-citric acid) elastomer coating	2.15 - 2.99	0.36 - 0.47
[68]		Pectin/polyethylnimin coating	0.43 - 0.56	0.18 - 0.20
		Pectin/polyethylnimin coating with microwave heating	2.3	0.72
[74]	Kenaf bast fibres	Urethane-based dilute solution (1.2 vol% fibre)	48.5 ± 8.1	
		Urethane-based dilute solution (2.4 vol% fibre)	33.4 ± 2.4	
[71]	Wood shaves	No treatment (wood content = 60 kg/m ³)	7	
		Impregnation into oil	<6	
		Coating with lime paste	8.5	
		Coating with cement-lime paste	10	
[67]	Flax shaves	No treatment	0.44	
		Coating with a cement-sucrose mix	2.5	
		Addition of 40% sucrose into the matrix	3.5	

Table 7. (cont.)

Reference	Kind of biomass	Treatment	Compressive strength at 28 days (MPa)	Flexural strength at 28 days (MPa)
[130]	Wood chips	Saturated with water	4.78 - 7.57	5.92 - 8.10
		Saturated with sodium silicate	6.82 - 9.85	7.51 - 10.15
[93]	Oil palm shells	No treatment	23.6	
		Concentrated borate solution	21.5	
		With 5 - 10 - 20 wt% sodium dichromate solution	20.89 - 21.33 - 24.33	
		With 5 - 10 - 20 wt% ferrous sulphate solution	20.39 - 20.14 - 19.67	
		With 5 - 10 - 20 wt% cupric sulphate pentahydrate solution	19.07 - 17.30 - 13.38	
		With 5 - 10 wt% acetic acid solution	18.90 - 18.82	
		With 5 wt% slaked lime solution	17.87	
		With 5 - 10 wt% poly(vinyl alcohol) solution	28.22 - 32.84	
[118]	Miscanthus stem fragments	No treatment (5 wt% based on cement mass)	25	~3
		Pretreated with acid prior to saccharification	<10	~3
		Pretreated with aqueous ammonia prior to saccharification	<10	~3
[131]	Coconut husks	No treatment	3.4 ± 0.52	
		Calcium chloride treated	3.7 ± 0.21	
[97]	Hemp shives	Replacement cement by binder A (NHL 3.5 - hydraulic lime)	0.11 - 0.18	
		Replacement cement by binder B (NHL 3.5 Z - hydraulic lime)	0.17 - 0.31	
		Replacement cement by binder C (NHL 2 - hydraulic lime)	0.10 - 0.22	
		Replacement cement by binder D (75% air lime+15% hydraulic lime+10% pozzolanic lime)	0.18 - 0.31	
[58]	Male date palm surface fibres	Curing concrete in water	15 - 30	
		Curing concrete in hot-dry climate	10 - 21	

Impregnations with latex and styrene-butadiene rubber or carboxylated styrene-butadiene copolymer emulsions were also applied on the surface of bamboo stem fragments and jute fibres [42]. These treatments helped to disperse fillers homogeneously in the cement matrix, to overcome the degradation in alkali medium and to reduce water absorption of the resulting concrete. Khazma et. al. coated flax shives with a poly(polyethylene glycol-co-citric acid) elastomer [66] or with pectin/polyethylnimin [68] to decrease filler water absorption and drying shrinkage with an improvement of mechanical properties. These treatments, however, delayed setting time of fresh concrete due to the presence of pectin [132] and increased the thermal conductivity of hardened concrete. The surface of kenaf bast fibres were treated with a urethane-based dilute solution to enhance the adhesion between fibres and cement matrix [74]. Concrete with coated kenaf fibres exhibited an improvement in cracking behaviour and hence enhanced durability. However, from a practical point of view, coating with such chemicals is complex on large scale, expensive and not environmentally-friendly.

Coating natural fillers by using the compounds which are already used for preparing conventional concrete was also described. Sisal and coconut fibres were immersed in a slurry of silica fume for 10 min and then air-dried for 15 min prior to incorporation in cement matrix [133]. The method was found to reduce embrittlement of concrete. It was reported that the addition of silica fume as an additive accelerated the cement hydration, filled the gaps in the cement structure and thus improved the mechanical properties of cement-bonded particleboard [33]. The suction of silica fume into pores of oil palm shell before adding to the mix enhanced the bond strength [133,134] and decreased the water permeability of concrete [14].

Bederina et. al. [71,73] treated wood shaves by spraying a paste of binder, including cement, lime and cement-lime pastes, on the shaves. Among these coatings, cement was the one giving the best results and this technique was previously claimed in two patents by Mouly [135–137]. Such coatings significantly reduced drying shrinkage, increased wood-cement adhesion and rigidity of wood, leading to an increase in mechanical properties of concrete and a reduction in dimensional variations. Coating flax fibres with a cement-sucrose mix revealed unexpectedly some positive results [67]. The presence of micro porosity in the coating layer resolved the problem of delay in setting time as well as drying shrinkage. A reduction in water absorption and thus an increase in compressive strength were also observed. In addition, the presence of sucrose enhanced the bond between aggregates and matrix but increased the thermal conductivity. The introduction of sodium silicate into wood chips by saturating them with a 100 g/L solution [130] improved the bond at cement-wood interface and

increased compressive strength. However, a loss of strength at long-term exposure was observed even with the samples stored at ambient temperature.

In order to reduce water absorption and protect fillers in alkaline environment, Juárez et. al. [76] used several organic water repellent substances such as linseed oil, paraffin wax, linseed oil/rosin (colophony) and paraffin/rosin for lechuguilla (from the algave family) leaf fibres. The treated leaf fibres exhibited a reduction in water absorption, good tension strength and ductility. Paraffin was found to be the most effective agent to protect biomass pieces from water absorption and alkali. Oil treatment, which was claimed to reduce water absorption, improve water repulsion and reduce the embrittlement process [9], was also performed on wood shaves as a comparison to treatment with pastes of binders [73]. The impregnation of wood shaves in oil helped to reduce drying shrinkage, but unfortunately, it caused a decrease in compressive strength of concretes.

The dimensional variations could be reduced, without significant influence on the compressive strength, by pulverization of organic hydrophobic components onto of pine wood granules such as polyethylene glycol or bitumen [138]. Bitumen also was reported to be used for coating cellulosic-containing materials such as straw to improve quality of the cement mix [139,140].

5.1.2 Chemical treatments

Chemical pre-treatments of biomass are very often used in all technical sectors where biomass is used. By either selectively removing biomass compounds (as in the case of paper making) or by chemically modifying either the surface or the interior of biomass materials (as in the case of the use of cellulose fibres for polymer composites), it allows to improve processing and the use properties of the final product, at the expense of the cost of the treatment. As stated, the cement hydration is usually inhibited by the extractives present in lignocellulosic plant species like wood. In consequence, the elimination of extractives might lead to substantial improvements of properties [33]. For this reason, it was also suggested that a simple way to improve fibre-matrix bond is to use materials containing less lignin as well as other chemicals that interfere with the bonds [10].

However, to remove lignin to improve concrete properties has several sides, one being that lignin is not too much interfering with cement setting and a second being that lignin is protecting the biomass filler against water intake, an effect known to cause difficulties during processing. Indeed, Tonoli et. al. [141] reported that a layer of lignin helped lowering water intake and acted as a physical/chemical barrier to prevent cement from migration into the fibre lumen. Consequently, the fibres were less vulnerable to mineralization. The use of lignin as a bio-preservation of wood was also described [142]. Thus, the presence of lignin should in general be a benefit.

Other extractives could have adverse effects on preparation and performances. The simplest method to remove water-soluble extractives is to wash/soak natural fibres in water. Cold water soaking of wood was shown to improve its compatibility with cement [33]. An extensive washing of wood pulp (cellulose extracted from wood) at high temperature was claimed to substantially remove the remaining “impurities” (mainly extractives and low molar mass hemicelluloses) in pulp [143]. 5 wet/dry water treatment cycles (wet: overnight at ambient temperature/dry: at 60°C for 4 h) were applied on flax nonwoven fabric to stabilise its dimension and also obtain composites with white cement with higher flexural strength and toughness [144]. After treating with boiling water for 2 h and washing until the colour of water was clear, coconut fibres/ropes became stiffer and tougher [145,146]. As a result, the fibre-matrix bond was enhanced and concrete tensile strength increased. Gunasekaran et. al. [84] compared behaviours of coconut shells (used as coarse aggregate with 10 mm-size range) treated with two water curing regimes, full immersion of shells in water and intermittent watering or with full air drying. Concretes made with such coconut shells treated with intermittent watering showed the highest bond strength, ultrasonic pulse velocities and compressive strength.

Alkali treatment is the most common method used to remove organic impurities as well as low molar mass hemicellulose and it was expected to improve fibre strength and fibre-matrix adhesion [9,32,132]. Alkali treatments can have many effects depending on alkali type, concentration and temperature. Sodium hydroxide aqueous solutions are used to remove non-cellulosic constituents like lignin and hemicellulose as in the treatment of wood to obtain cellulose pulp fibres [31], to dissolve cellulose when its concentration is low (6-9%) and temperature is below ambient [147] and to modify cotton fibres for textile applications (mercerization process) when concentration is in the range of 18-32% NaOH concentrations at 25-40°C [148]. The surface morphology of plant biomass pieces is also changed. Thus, alkali treatment produces plant fillers with improved thermal stability and removes surfaces debris and parts of lignin and hemicelluloses [149,150]. In addition, alkali treatment leads to fibrillation of the internal cellulose fibres due to the removal of hemicellulose which acted as a binder between them, thereby increasing the effective surface available for contact with cement matrix. The hydroxyl groups available on the surface of cellulose factions are responsible for fillers and cement bond. Various concentrations of alkali solutions (from 0.5 % to 10%) were tried on jute [42], coconut coir [149,151], and hemp fibres [61,132] at ambient temperature. After alkali treatment, fibres were stronger, but their tensile strength changed depending on NaOH concentration [151]. The strength decreased if severe alkali conditions were applied. Concrete prepared with alkali-treated fibres exhibited a reduction in water absorption, better tensile

strength and a good fibre-matrix bond. To compare with the alkali treated fibres (6 wt% at room temperature), cortical hemp fibres were treated with a 1 wt% AlCl_3 solution at room temperature [132]. In comparison to the untreated fibres, the chloride aluminium treatment improved 7% in flexural strength of the composites, while that value was 39% for alkali treatment. The addition of NaCl and Na_2CO_3 in NaOH solution helped to clean oil and waxes from cotton wastes and allowed them to be homogeneously dispersed in the mix with limestone-cement-water [48]. However, the remaining of salts after treatment may cause salt damage of concrete if the washing of fibres was not done carefully. When treating with 10% NaOH at 100°C or higher, lignin was also removed [104,152]. Cooking of hemp core fibres (short, lignified fibres extracted from hemp) with NaOH in ethanolamine solvent at 180°C was claimed to be effective to remove lignin, hemicellulose and extractives, and to improve the fibre-matrix interaction [152].

Concrete without biomass treated with silane emulsions absorbed very little water and could be considered to be durable in an aggressive environment [153]. It is known that the use of organo-functional silane coupling agents reduced the hydrophilic behaviour of natural fillers [9,49,154,155]. For example, conventional bleached and unrefined eucalyptus kraft pulp cellulose fibre surfaces were modified with methacryloxypropyltri-methoxysilane (MPTS), aminopropyltri-ethoxysilane (APTS) and n-octadecyl isocyanate [49]. MPTS reduced the hydrophilicity and lead to high mechanical properties. In addition, MPTS improved dimensional stability of composites and durability, and also decreased the final water/cement ratio. The treated cellulose fibres were free from cement hydration products. In contrast, APTS increased the hydrophilicity, reduced strength and durability and accelerated mineralization, leading to higher embrittlement behaviour of cement.

The modification of the surface of pine pulp fibres with titanium alkoxide as coupling agent was carried out at Commonwealth Scientific and Industrial Research Organization (CSIRO) in the 1970s [10,156]. The results showed that the matrix bonding to wood fibres during processing was improved.

The wood-cement compatibility also increased when pine sticks were treated with copper-chromium-arsenate and chromic acid [33,127]. There was an increase in the pull-out resistance of pine sticks embedded in cement and in flexural toughness of wood-cement composites.

After treated with a solution of 0.25% sodium alginate ($\text{NaC}_6\text{H}_7\text{O}_6$), coconut fibres/ropes were soaked in 1% CaCl_2 and then dried at 70°C [145,146]. The treatment leads to the reduction in the ultimate tensile strength of fibres and the fibre-matrix bond. Various solutions (with 16 treatments) including concentrated borate, 5-10-20 % sodium dichromate, 5-10-20% ferrous sulphate, 5-10-20%

cupric sulphate pentahydrate, 5-10 % acetic acid, 5% slaked lime and 10-20% poly(vinyl alcohol) solutions were used to treat coarse oil palm shells for preparing lightweight concrete [93]. The 20%-PVA-treated-shell filled concrete presented higher durability in tested conditions and good compressive strength. The sulphur attack caused the reduction in compressive strength and the slaked ($\text{Ca}(\text{OH})_2$) lime-treated shell increased the formation of cracks on the concrete surface.

The modification of the capacity of biomass to uptake water is another strategy which was tested to preserve service life of fibres in cement matrix. Several complicated attempts to reduce moisture absorption of fibres were reported. These methods are based on treating natural fillers prior to be embedded into cement matrix. Already in 1936, Handl and co-worker tried to mineralize wood chips by dropping them in aluminium sulphate solutions [157]. Buys [158] improved the process of manufacturing light cellulosic-cement articles by treating wood with ferrous sulphate solution to reduce its porosity. Mineralization process was also used to remove sugars from wood, rendering the material completely inert and no longer susceptible to rot or be damaged by termite [110]. Wood pulp (cellulose fibres extracted after a cooking process removing most lignin and hemicellulose) was made more stable in a cement medium by a treatment aimed at reducing its swelling in aqueous and alkali media [159]. The treatment included dispersion of pulp in water, impregnation in a solution of titanium and/or zirconium chelate and subsequent heating to induce a cross-linking reaction. The treated pulp increased its hydrophobicity, dispersed well in the cement matrix and helped to improve flexural strength and modulus of the resulting products. Samal et al. [160,161] performed several chemical treatments including cyanoethylation and cyanoethylation followed by grafting with acrylonitrile or methyl methacrylate, dinitrophenylation and benzylation-acetylation. These treatments brought a significant reduction in hydrophilicity of pineapple leaf fibres. Acetylation on sisal fibres reduced their equilibrium moisture content, but also their tensile strength due to the loss of hemicelluloses in fibres during acetylation [162]. Together with the reduction in water absorption, thermal stability as well as bulk mechanical properties of pineapple leaf fibres could be improved by grafting copolymerisation of acrylonitrile onto fibres using $\text{Ce}(\text{IV})$ and *N*-acetylglycine combination as initiator at the temperature range 40-60°C or $\text{Cu}(\text{II})\text{-IO}_4^-$ initiated graft copolymerisation of methyl methacrylate [163]. Four other coupling agents studied by Singh et. al. [164] are *N*-substituted methacrylamide, γ -methacryloxypropyl trimethoxysilane, neopentyl-(diallyl)oxytri(dioctyl)pyrophosphato titanate, and neopentyl-(diallyl)oxytriacyl zirconate. They were used to hydrophobize sisal fibre surfaces via the addition of long hydrocarbon chains. Furthermore, these coupling agents penetrated the cell wall through surface pores and deposited in the interfibrillar regions and on the surface, restricting further ingress of moisture. A new direct

fluorination treatment has been reported to reduce wood hydrophilicity [165]. A mixture of spruce and Douglas wood species from sawmill co-products was treated with pure F₂ gas under controlled pressure and temperature. The result showed that treated wood reached the water equilibrium point faster than the untreated one and direct fluorination reduced water content in the treated wood from 9 to 30 wt%, dependent on the tested relative humidity. Although this method has only been tested with polyester composites (with improvement in tensile and flexural strengths, better adhesion, and reduction in capacity to absorb water), it may be considered as a useful treatment applying for inorganic matrix.

Other treatments which have been applied on fibres include anti-microbial treatments to prevent plant-based filler degradation and enhance the overall durability [74] or treatments with cationic starch and fly ash to improve biomass-based filler dispersion during mixing [52,166] and effect on cement set retarding [167]. Saccharification by two treatments with either 2% H₂SO₄ at 121°C or with 33% aqueous ammonia at ambient temperature and enzymatic cocktail (cellulase, β-glucosidase and xylanase) at 50°C was carried out on *Miscanthus x giganteus* stem fragments and then the enzymatic residues were incorporated into the cement matrix [118]. However, the results revealed a delay in setting time of fresh concrete and a decrease in mechanical properties of hardened concrete.

5.1.3 Physical treatments

Apart from the coating and chemical treatments mentioned, some physical modifications were also tested to improve the physical and mechanical properties of biomass-based fillers. By the action of heat such as drying in oven or fire on wood shaves [71], bamboo [36], or thermally treated wood granules by autohydrolysis [138], swelling of these fillers can be reduced and part or all their hemicellulose fractions degraded. As a result, fillers become less susceptible to microorganism attacks. Thermal treatment can also improve the adhesion strength between fibres and cement matrix. A combination of compression and temperature (120, 160 and 200°C) was tested [41]. Sisal fibres were heated up to certain temperature and kept for 5 min before compression was applied. The compression force with a rate of 15 N/min and a maximum load of 90 MPa on the fibres (calculated based on the estimated area of fibres) was maintained for 5 min in the perpendicular direction to the fibre length. The treatment led to an increase of sisal fibre stiffness and a decrease of moisture absorption.

The carding process is disentangling, mixing and aligning fibres. By carding flax fibres, pectin and hemicellulose were partly removed, more elementary fibres were produced and durability in alkali

was improved [69]. Concrete produced with these carded fibres exhibited higher elasticity modulus, but fresh concrete showed lower workability.

5.1.4 Mixed treatments

In some cases, a combination of two or more treatments was applied to fibres. Refining of pulp fibres (a term coming from paper making industry, which is a strong mechanical treatment in the presence of water and metallic bars) make them more compatible with various organic and inorganic matrices by producing a large accessible surface area improving fibre-to-fibre or fibre-to-matrix bonding [10]. Li [168] reported a process to treat sisal fibres at high temperature with 50 % NaOH solution followed by a chemical coating. The treated fibres showed an enhanced alkali resistance, were easy to disperse and were suitable to be used as reinforcement in concrete. Jute fibres were also treated in alkali to remove some organic compounds prior to be immersed in diluted emulsion of carboxylated styrene butadiene copolymer for coating [42]. The addition of tannin in the polymer emulsion promoted homogeneous distribution of cement in concrete. The obtained concrete showed a significant decrease of water absorption and an improvement in compressive and flexural strength.

After being impregnated with calcium or barium salt solutions, hemp shives was coated with a sodium silicate solution before being incorporated into the cement matrix [169]. Francis [170] treated wood pieces with sodium silicate solution after drying the wood pieces so that they became inert in the cementitious environment, preventing reactions between wood, water and cement, enabling further use in concrete.

Oilseed flax fibres were passed several chemical treatment steps in order to improve the interface between natural fibre and inorganic matrix, the stability in alkali environment and to reduce hydrophilicity before being used in cementitious composites [171]. The fibres were pre-treated by de-waxing in boiling acetone for 45 min and then with 5 wt% NaOH solution for 40 min. After being neutralised, rinsed and dried, pre-treated flax fibres were either coated with ZrO₂ solution or silane emulsion (APTS or MPTS). The ZrO₂ and silane coated fibres showed an efficient improve in against alkali degradation and hydrophobicity.

5.2. Matrix modifications

Reducing the alkalinity of cement matrix is another option to increase the durability of biomass-based materials. By adding by-products such as fly ashes [42,54,60,76,77,134,172], silica fume [56,64,70,134,172], pumice [173], rice husk ash, blast furnace slag and metakaolin [46,52,144,174–176] to Portland cement, the alkalinity of binders can be reduced. The results demonstrated that this

is as an effective method for preventing fibre degradation and improving the durability of composites. In the case of fly ash, it resulted in a denser matrix with reduced humidity ingress, preventing thus fillers from deterioration. Moreover, the advantage of adding fly ash into the binder is that it can react with $\text{Ca}(\text{OH})_2$ generated from the hydration of Portland cement, leading to the reduction of $\text{Ca}(\text{OH})_2$ migration into fibre lumen and cell walls, and thus avoid embrittlement behaviour of cementitious products [33]. It also increased the ease of mixing.

The addition of some accelerators for cement hydration into matrix also improved the compatibility of wood-cement-water systems and the flexural strength of cement composites [33]. Some of the most common accelerators tested are CaCl_2 [37,131], activated charcoal, SnCl_2 , FeCl_3 , AlCl_3 [33] or MgCl_2 [177]. By replacing 5 – 10 wt% of regular binder with microsilica or sodium silica solution, the binder has shown good binding capacity with bio-based filler and an enhancement in compressive and flexural strengths [178]. Nozahic [96] added cellulose ether with the amount from 0.5 to 1.5% of cement amount to the mixture to improve the adhesion between hemp and sunflower stem granules with cement. The addition not only enhanced the interface between hemp and binder but also lead to an increase in elastic modulus and resistance at 5% of deformation.

Despite the fact that the presence of sugar in biomass can cause some problems for cement hydration, as mentioned before, the addition of sucrose in large quantity (ca. 40% of cement) was tried by Khazma et. al. [67]. The results showed that the mechanical properties of concrete were increased, setting time of fresh concrete was reduced and behaviour in water was improved. This method is simpler than coating flax with cement-sucrose mixture.

5.3. Other modifications

Apart from the modifications of fillers or cement matrix to overcome the disadvantages mentioned in previous sections, several other possible solutions have been suggested. Exposing Portland cement to carbon dioxide by CO_2 injection can reduce the setting time [33,179–181]. By reducing cement alkalinity, the carbonation process mitigates the degradation and mineralisation of fibre constituents and thus increases the durability of concrete composites. The interface between cellulose fibres and cement improved, leading to the reduction in permeability.

Instead of mixing components in dry state, Li et. al [86] reported that wet mixing resulted in a better dispersion of fillers. A projection process has been proposed as a modification method for concrete fabrication [87]. The process induced a better compaction, higher density and hence, increased thermal and mechanical properties of the resulting concrete. Nguyen and co-workers [90] optimized

pre-cast building elements and found that the compression during casting lead to better mechanical performances of concretes. However, the higher density caused an increase in thermal conductivity.

6. Conclusions

As seen in this review, many methods have been proposed to overcome the difficulties arising in preparing biomass-based concrete. These difficulties are directly linked to the structure and composition of lignocellulosic biomass, whatever it is coming from. It is very clearly demonstrated that several components of biomass, like soluble sugars or low molar mass hemicelluloses have adverse effects on the preparation and performances of concrete. This open the way to either select biomass sources minimizing these drawbacks or tailoring biomass for having improved sources of biomass-based materials. However, even “optimized”, biomass will always be hygroscopic, have a light structure with many hole (which is of course one of the interests for using it), be of low stability and have poor mechanical properties. The many methods tested to overcome or at least decrease these effects have been reviewed in this article. A large proportion of these methods are effectively helpful in easing the concrete preparation and leading to better final materials. However, most of them, if not all, have little practical value since they are either impossible to be implemented because of the use of chemicals which are not environmentally-friendly or much too expensive. Cost is the main driver since the replacement of mineral aggregates by biomass-based fillers must be at no cost (or at least with a very little increase). To find a simple, cheap, environmentally-friendly method to prepare biomass-based concrete with good mechanical properties on the long term is still a big challenge.

Long term preservation of properties is a very important issue which seems to have been mostly neglected. Very few studies mentioned the service life or long-term durability of this class of materials.

A last aspect, never mentioned in scientific publications, is the need to transport the biomass-based material from its production place to the concrete factory. If the distance is too long, the environmental advantage of using biomass will be ruined by the environmental cost of transportation.

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Captions for the Figures

Figure 1. Spruce bleached sulphite pulp fibre observed by scanning electron microscopy. Top: this fibre is the wall of a single cell, where the nucleus was in the central part. What we see here is the outside part of this fibre. Bottom: the picture is showing the array of microfibrils of less than 100 nm thickness attached to the surface, surrounding a pit opening (Reprinted with permission from the PhD dissertation of Nuno dos Santos [24]).

Figure 2. A hemp-based house built in Florida (with permission from Bob Clayton, Florida, USA) [103].

Figure 3. Coconut reinforced concretes: a) a concrete block, b) the concrete panels and c) the house built from them (with permission of Nguyen Tan Khoa and his supervisor (Dr. Le Anh Tuan) [104].

Figure 4. Various applications of mountain pine wood concretes [105]. With permission from Pasca, S & Hartley, ID 2012, 'Beetlecrete – An attractive solution to mountain pine beetle epidemic', Proceedings of International Inorganic-Bonded Fiber Composites Conference (IIBCC 2012), 10-14 September, 2012, Acton, Australia. (Available from: www.proceedings.com. Item #20276)

Figure 5. a) Miscanthus-based mix and block (author's work) and b) a miscanthus based noise barrier and (c) a house built with miscanthus concrete [106]. With authorisation of asbl ValBiom, Croix du Sud 2, bte 11, 1348 Louvain-la-Neuve, Belgium.